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OF

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CHEMICAL TECHNOLOGY
AND ANALYSIS
OF
OILS FATS AND WAXES

BY

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CONSULTING AND ANALYTICAL CHEMIST, AND CHEMICAL ENGINEER
EXAMINER IN "SOAP MANUFACTURE" AND IN "FATS AND OILS" TO THE
CITY AND GUILDS OF LONDON INSTITUTE

FIFTH EDITION, ENTIRELY REWRITTEN AND ENLARGED

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IN THREE VOLUMES
VOL. I

WITH ILLUSTRATIONS AND NUMEROUS TABLES

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PREFACE TO THE FIFTH EDITION

During the few years which have elapsed since the fourth edition of this work was published, great strides have been made in the industry of oils and fats. By laying under contribution the latest discoveries of pure science and translating them effectively into practice, a leap has been made in advance of all the limitations which, up till recently, science, and apparently even nature itself, had drawn.

Whereas a decade or two ago chemical *analysis* pointed out the way to technical development, and purely scientific discoveries appeared to have comparatively little influence on the progress of our industries, the order is now reversed. In its influence on the advance of the oils and fats industries pure *science* has stepped ahead, and it is now the turn of analytical chemistry to follow in the wake of progress and to detect in the finished article the achievements of technical work.

There have not, therefore, been wanting voices declaring that the analytical armoury of recent years has become obsolete and that fat analysis has to begin afresh. I do not share this opinion. Just as little as the discovery of radium and the latest researches on the constitution of the chemical elements have been able to render superfluous the methods of mineral analysis, so little will the present analytical edifice of the oil and fat industries be consigned to the limbo of things that were.

The forward strides which technical effort has made will only contribute to quicken the pace of the discoverer of new analytical methods and lead to a deepening of the foundations of the analytical processes already available. Thus a timely warning has been raised against the danger which threatened fat analysis at the hands of those who, by thoughtless application of very valuable methods, unwittingly degraded fat analysis to a hollow formalism.

In view of the state of transition through which fat analysis is passing at present, I would have preferred to allow some little time to elapse before a new edition was published, but as the last edition is completely exhausted, the appearance of the present work could not be delayed.

In the present volume no more than an attempt could therefore be made to show where analytical processes will have to step in to assist the analyst in unravelling the mysteries which the technical chemist is now able to present to him. Some methods which are being worked out at present in my laboratory have been given in a tentative fashion only, as they are still being subjected to crucial tests.

The amount of labour involved in the production of the present edition has been so great, that it was found impossible to publish the work as a whole, as was done before. The present volume, as in the last edition, deals with the chemistry and the analysis of oils, fats, and waxes. Although every endeavour has been made to compress the subject-matter and eliminate what has become antiquated, it has been impossible to avoid a very considerable increase in the bulk of this volume.

In order to facilitate the rapid appearance of the work no index has been added; this is replaced, to some extent, by a very comprehensive list of contents, which may suffice until the third volume supplies a full index to the whole work. The subject-matter of Volume II. being already in the press, no avoidable delay will occur in the appearance of the second and third volumes.

J. LEWKOWITSCH.

71 PRIORY ROAD,
LONDON, N.W., *July* 1913.

PREFACE TO THE FOURTH EDITION

THE rapid exhaustion of the third edition of this work and the favourable reception which has been accorded to the German and French editions on the Continent have encouraged me to widen the scope of the technological sections of this treatise. This has necessitated the complete rewriting of the work and its division into three volumes.

The arrangement of the subject-matter in Volume I. has not undergone radical changes, and it need only be said that all new investigations, some of which were carried out in my own laboratory, have been fully incorporated with, and critically interwoven in, the old text. The fact that the same material had to be presented in the German and French languages has, I trust, contributed in some degree to the elimination of ambiguities in the diction. It has also enabled me to present the subject-matter in a more lucid manner and to rearrange it in strictly logical sequence. More attention than in previous editions has been paid to the historical development of analytical processes. This led to the correction of many wrong, although currently accepted, statements.

The monographs which form the bulk of the second volume have been greatly expanded on the basis of practical experience gained by me in the course of recent visits to the most important establishments in the United States of America and on the Continent, especially in the south of Europe. An endeavour has been made to summarise the modifications of the several processes adopted in different establishments, and to present, as it were, an ideal sequence of manufacturing operations, combining the most advantageous features of working. To illustrate wherever possible the commercial importance of the oils, fats, and waxes, statistical data, drawn from the most reliable sources, have been added. The analytical portions attached to each of the monographs have been fully brought up to date, and have been amplified by a large amount of original investigations of a technological character carried out during the last few years in my laboratory (as a reference to the sections on "Olive Oil," "Cod Liver Oil," "Lard," "Butter Fat," "Beeswax," and others will show). In order to render this second volume more useful, an index of botanical and zoological names has been affixed.

The additions to the third volume are proportionately the greatest. This is caused not only by the introduction of some new sections (such as "Emulsified Oils," "Fatty Acid Industry," "Technology of Waxes") but also by the allocation of much more space to the description of manufacturing operations. The new manufacturing processes which have been introduced lately have been fully recorded. The endeavour to be as concise as possible has led to the relegation of less striking progress to the footnotes, which give a complete reference to the patent literature of the last decades.

Whilst every care has been taken to render the work as free from errors as possible, it would be almost too much to hope that none have crept in. I should therefore be grateful to my colleagues if they would assist me by pointing out to me any errors they should happen to find.

J. LEWKOWITSCH.

71 Priory Road,
London, N.W.

PREFACE TO THE THIRD EDITION

THE present work is nominally the third edition of my "*Chemical Analysis of Oils, Fats, and Waxes and the Commercial Products derived therefrom.*" Practically it is a new work, for not only has the last edition been entirely rewritten, but it has also been expanded into a chemical technology of the subject. This extension of its scope will justify the change of title.

The analytical portion, which in the previous editions constituted the most prominent feature of the work, now forms the main portion of the first volume of this book, whilst the technology of the subject has been relegated to the second volume.

The first three chapters of Volume I. form a general introduction to both the analytical and technical portions of the work. Whilst I have given the amplest consideration to the scientific principles underlying the analytical and technical operations, I have kept prominently in the foreground the practical purposes which this work is intended to serve. Very frequent references have therefore been made in these chapters to the analytical methods and technical processes which form the main subjects of the present work. This especially holds good of the second chapter treating of the theoretical side of the hydrolysis (or saponification) of oils and fats, and also of that portion of the third chapter which deals with the hydrolysis of soap. I hope that the new form in which the matter is presented may serve as an outline of the theory underlying the large industries described in Volume II.

The great impetus which analytical investigations have given to the development of this branch of chemical technology rendered it necessary to devote ample space to the analysis of oils and fats. Hence the technical methods of preparing the raw material which is subjected to chemical analysis in the laboratory have been transferred to the second volume.

The chapters which in the former editions of this work dealt with the analysis have been entirely recast, and rearranged in such a manner as to provide all the information required by the analyst and by the technical chemist in a synoptical form. With this object in view I. have presented all recorded numbers and observations as far as possible in tabular arrangement. The division of the most important numerical values into "*constants*"[1] and "*variables*," outlined in my *Laboratory Companion*, has been strictly carried through in this work, as I consider that only the constants furnish values which are characteristic of the nature of an oil or fat, whereas the variables are merely determinants of their quality. I have further endeavoured so to arrange the analytical portion as to set before the reader a systematic course of analytical examination, the several methods being described in logical sequence. For the sake of convenience I have briefly recapitulated this systematic course in Chapter XI., illustrating it by means of a few examples.

It need hardly be pointed out that all the new analytical matter which has accumulated since the publication of the last edition has been embodied in the work. Obsolete methods and obviously unreliable processes have been omitted, my object being to offer, as far as I am able, to the analyst and technical chemist guidance and assistance such as the reader looks for in a work of this kind. The ideal course of presenting one analytical process only is not yet feasible. Therefore, I have ventured to criticise somewhat freely when several processes had to be described, and to point out certain defects. Wherever possible I have added to my critical remarks suggestions for improvement. I feel that the weight of some practical experience attaches to such criticism as I offer, for the great majority of the methods described here have been tested repeatedly by myself and a number of younger colleagues in my laboratory during the last twenty years.

In the last chapter of the first volume I have collated a number of methods and suggestions which up till now bear a strictly scientific character, but may in the future be worked out into useful analytical processes.

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[1] In the present edition the term "constants" has been replaced by "characteristics."

The second volume is specially devoted to the technology of oils and fats. A detailed description of each individual raw material has been given in Chapter XIV. I have summarised the knowledge we possess at present of each individual oil, fat, and wax, describing its occurrence, mode of preparation, mode of purification, chemical composition, examination and detection of adulterants, and pointing out its technical uses. Thus this chapter furnishes, in a concise form, a series of monographs of all known oils, fats, and waxes.

The manufacturing processes practised in the oil and fat industries have been enumerated in systematic order in the last two chapters. Chief stress has been laid on the exposition of the principles on which the individual industries are based. Wherever it appeared necessary I have added illustrations of apparatus. Most of these have been engraved especially for this edition, and those that are not new have been mostly re-drawn. The processes described are those which I know from my own experience to be in practical use at the present day. Antiquated processes have only been touched upon in the briefest manner, when their description was deemed necessary for the proper understanding of more modern methods. The patent literature has, therefore, only been referred to in so far as it furnishes information of practical importance or contains suggestions for industrial application. It is, of course, impossible to teach the art of successful manufacture, for this must be learnt in the school of experience. In this section of the work the scope for criticism naturally became restricted. The reasons for this are obvious. Moreover, the difficulty of judging is enhanced by the fact that a manufacturing process, which is carried out with advantage in one factory, proves not infrequently a failure in another.

Throughout the two volumes of the work there will be found interspersed a considerable number of original notes which I have not published hitherto.

In order to increase the utility of the book I have given numerous cross-references in its pages, and have added a somewhat comprehensive index of subject-matter.

J. LEWKOWITSCH.

71 Priory Road,
London, N.W.

By Dr. J. LEWKOWITSCH

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CHAPTER I

ERRATA AND ADDENDA

age 13, line 14 from top, add " *Berichte*, 1913, 1655."
,, 26, line 13 from top, add " For the action of concentrated sulphuric acid on laurin cp. p. 75."
,, 28, line 8 from top, for " C_{31}" read " C_{30}."
,, 29, line 23 from top, for " 14,619 " read " 1,4619."
,, 29, line 3 from bottom, for " $(O.C_{22}H_{39}ClO)_2$" read " $(O.C_{22}H_{39}ClO)_3$."
,, 34, line 24 from top, for " $(O.C_{17}H_{27}O)$ " read " $(O.C_{14}H_{27}O)$."
,, 35, line 11 from top, for " 57·3 " read " 51·3."
,, 40, insert at end of page, " roots of *Polygala Senega* and the."
,, 61, insert at end of line 22, " Selenium chloride and tellurium chloride act similarly. *H. Klopstock*, German patent 260,916."
,, 92, add to footnote 1, " K. G. Falk, *ibid.*, 1913 (35), 601, 616."
,, 116, line 2 from top, for " wax " read " waxes."
,, 133, line of footnote 1, for " $C_{16}H_{38}$" read " $C_{16}H_{31}$."
,, 146, lines 2 and 6 from top, for " ÷ " read " +."
,, 152, line 17 from top, for " 152 " read " 142."
,, 154, line 11 from top, for " 152 " read " 142."
,, 193, line 3 from top, for " $C_{18}H_{31}O_3$" read " $C_{18}H_{32}O_2$."
,, 202, line 3 from top, for " $CH_3.(CH_2)_3.CH=CH.CH=(CH_2)_9COOH$ " read " $CH_3.(CH_2)_3.CH=CH.CH=CH(CH_2)_9COOH$."
,, 209, line 9 from top, for " g." read " grms."
,, 236, line 6 from bottom, add " For chloroarsenobehenolic acid cp. Emil Fischer and Georg Klemperer, *Therap. d. Gegenwart*, January 1913."
,, 274, line 11 from top, for " glacial acid " read " glacial acetic acid."
,, 326, footnote 1, for " Loewensteen " read " Lowenstein."
,, 340, line 26 from top, for " Njore-Njole " read " Inoy kernel."
,, 388, line 11 from top, for " Njore-Njole " read " Inoy kernel."
,, 411, last line, for " Njore-Njole " read " Inoy kernel."
,, 449, lines 4 and 5 from bottom: The " International Standard Methods 1911 " (cp. Vol. III. " Glycerin Manufacture ") adopt the figure 0·03609.
,, 481, in headline, for " Aumené " read " Maumené."
,, 576, line 1 from bottom, after " is absent " add " if blackening is noticed."
,, 590, line 1 from bottom, second column, for " 10 " read " 90."
,, 612, add to footnote 3 " Cp. C. S. Reeve and R. H. Lewis, *Journ. Ind. Eng. Chem.*, 1913, 293."

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CHAPTER I

CLASSIFICATION OF OILS, FATS, AND WAXES—PHYSICAL AND CHEMICAL PROPERTIES OF OILS, FATS, AND WAXES

THE fatty oils (liquid fats), solid fats, and waxes which are the subject of this treatise are found ready formed in vegetable and animal organisms, from those consisting of a single cell only up to the most highly organised plants and animals. The discussion of the theories put forward to explain the " biochemical " synthesis of oils, fats, and waxes in plants and animals lies beyond the scope of this work, and the reader must be referred to text-books on physiology for further information, all the more so as the opinions of physiologists differ. It may, however, be pointed out that it appears to be certain that oils and fats and also waxes are formed from carbohydrates. *Luca* is of the opinion (which is not shared by other physiologists) that in the olive fruit mannitol is transformed into oil,[1] and *Müntz* showed that glucose, saccharose, and starch seem to play in rape seed, poppy seed, and linseed, the same part which mannitol plays in the olive. In the animal organism also fat is formed from the carbohydrates ingested with the food. If the fats are synthesised in the organism by means of enzymes, from fatty acids[2] and from glycerol,[3] it would follow that both must be first formed individually. In the case of fats which are ingested with the food in large amounts, the fats are stored as such in the body tissues to serve as a reserve in case of need. If such fats are taken in smaller quantities they may, like carbohydrates, be oxidised to carbon dioxide and water.

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[1] According to Scurti and Tommasi, *Ann. Reale Stazione Chim.-Agrar. Sperim. di Roma*, 1910 (4), 253, an ethereal extract of young, unripe olive fruits consists almost completely of an alcohol—"oleanol," $C_{31}H_{50}O_3$ (the presence of which in the leaves of the olive tree has been proved by Canzoneri, as also by Power and Tutin), which is converted into oleic acid. Hence, the formation of glycerides in the mesocarp of the olive fruit would appear to take place on lines differing from the formation of oils and fats in oleaginous seeds. Similarly the alcohol "ligustrol" (in *Ligustrum vulgare*) is stated to be converted into erucic acid (cp. Scurti and Fornaini, *Ann. Reale Stazione Chim.-Agrar. Sperim. di Roma*, 1911 (5), 103 ; 223 ; 1913 (6), 29 ; 39).

[2] With regard to the formation of saturated fatty acids from "phytol" (from chlorophyll) cp. Willstädter, *Chem. Zeit.*, 1911, 1342.

[3] According to G. Embden, E. Schmitz, and K. Baldes, *Biochem. Zeit.*, 1912 (45), 174, glucose leads in the first instance to an optically active glyceraldehyde, which is to some extent converted into glycerol, and thus constitutes the main source for the formation of glycerol in the animal organism. This theory would assume that fat in the animal organisms is formed from its elements as it were, and not, as some investigators assume, that all the fat is supplied in the food.

It is quite admissible in the present state of our knowledge, to assume that the fats deposited in the body tissues are hydrolised in the process of digestion and are then transported separately in the form of fatty acids and glycerol through the membranes, to be synthesised again to fats. If this view be correct, then the problem of the formation of fats and oils is only shifted but not solved.

To the analytical and technical chemist the study of the influence which soil, climate, etc., have on the composition of the individual vegetable oils and fats is, however, of considerable importance; in addition to these factors, the influence which the food, race, and age of the animal have on the composition of the animal oils and fats must be considered. These factors will be discussed in Vol. II. in the introduction to the section "Animal Fats," as also under the headings of the individual fats described there. In the organisms there occur a number of enzymes (diastase, lipase, etc.) which probably effect the synthesis of oils and fats by a series of reactions which follow somewhat rapidly one upon another. Hitherto very little is known with regard to these changes; they appear all the more complicated as enzymic reactions seem to be reversible ones,[1] and synthesis and hydrolysis appear to take place simultaneously or to follow each other, especially in the higher animal organisms, in a kind of rhythmic succession (cp. Chap. II.). In the present treatise the synthesis of fats by means of "ferments" is of much less importance than their hydrolysis by enzymatic processes, as only these have acquired technical importance. The hydrolysis based on enzymatic processes will be dealt with from the theoretical point of view in Chap. II. of this volume, and from the technical point of view in Vol. III. Chap. XV.

The vegetable waxes occur as exudations on the leaves, stems, and fibres of plants. It is unknown how their formation takes place. The liquid waxes appear to be formed much in the same manner as the marine animal oils, and their chemical composition is influenced by the same factors which produce variations in the composition of animal oils and fats derived from different individuals of one and the same species. As regards its formation, spermaceti would seem to owe its origin to similar physiological causes.

The insect waxes constitute mostly exudation products. In support of the view that they are formed from carbohydrates may be adduced the fact that beeswax is produced in much larger quantities than usual by the bees, if they are fed on dextrose, lævulose, and also cane-sugar.

Under the term oils, fats, and waxes (liquid and solid) are comprised in this work all those naturally formed substances which consist mostly of glycyl-, or other esters of the higher members of the several series of fatty (aliphatic) acids, with which in some cases notable amounts of the free fatty acids and the free alcohols themselves are admixed.

In the present state of our knowledge, a strictly systematic classification of oils, fats, and waxes is not possible. In older text-books, various attempts have been made to establish several classes or groups, differing chiefly by some physical properties. Thus the consistence (see Chap. V.) has been made the basis of a classification into oils, butters, and solid fats, but such a principle of classification is inadmissible, as the consistence depends on the mean annual temperature; thus cocoa nut oil is a solid fat in a temperate climate, whereas, in its place of origin, it is of an oily consistence, as its name implies. It would be easy to multiply examples of this kind. Again, some authors have endeavoured to differentiate the fats into several groups on the strength of some prominent chemical property of the fatty oils, such as their drying power; but here also the old adage "*natura non facit saltus*" proves too strong for an artificial classification, inasmuch as there exist a number of fatty oils, occupying an intermediate position, so that they might be classed under two or more heads.

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[1] Cp. A. S. Loevenhart, *Amer. Journ. of Physiol.*, 1902, 331, and below, Chap. II. Vol. I. Cp. also Lewkowitsch, "Les Corps gras (Industrie et Analyse) Conférence," *Société chimique de France*, 1909, xviii.

A classification of the vegetable oils and fats based on the plant families from which they are derived must be entirely out of the question. It is true, the oils derived from *Cruciferæ* and *Rosaceæ* are nearly related to each other; but on the other hand, the *Euphorbiaceæ* yield fatty products of such different characters as croton oil, castor oil, tung oil, curcas oil, and vegetable tallow; and the *Sterculiaceæ* contain such widely different fats as sterculia oil and cacao butter. The fact that the African palm tree yields in its fruit flesh and in the fruit kernel two entirely different fats, viz. palm oil and palm kernel oil (cp. also "Aouara Oil," Vol. II. Chap. XIV.), would seem to render hopeless any attempt to introduce a classification of this kind. The same would hold good of a similar classification of animal oils and fats. To give only one illustration, in the case of mammals the body fat is entirely different from the milk fat of the same animal.

A rational classification must be founded on distinct physical, as well as chemical properties. Therefore, the attempt is made in this treatise to base the classification, as far as possible, on such physical and chemical differences as can be readily ascertained by means of analytical operations.

Such distinct chemical differences can be established between oils and fats on the one hand, and waxes on the other.

Considered chemically, oils (fatty oils) and fats (solid fats) are the neutral glycerides of fatty acids, whereas waxes are esters formed by the union of fatty acids with alcohols not belonging to the glycerol series. It should be noted, however, that this chemical difference does not always find a ready expression in common parlance. Thus, *e.g.* Japan wax consists chiefly of glycerides, and would more properly be termed Japan tallow. On the other hand, sperm oil must be classed, according to its chemical constitution, amongst the waxes. (It is desirable that the old misleading terms should be gradually deleted from chemical treatises.)

The term *wax* is frequently used as a generic name for a number of solid hydrocarbons, *i.e.* mineral waxes. Since a full description of these does not fall within the purview of this work, they will only be referred to in connection with the analysis of the fatty products with which they may be admixed (as in the manufacture of certain candles, polishes, and similar products).

The most convenient classification of fatty oils and fats for practical purposes, appears to be given by arranging them according to the magnitude of the **iodine value**. This principle leads, without undue forcing, to a natural subdivision into liquid fats—*oils*—and solid fats—*fats*—the former being differentiated from the latter by their considerably higher iodine values. An arrangement based on the magnitude of the iodine value would include the older system of classification according to "consistence." Inasmuch as the magnitude of the iodine value stands in close relationship to the absorption of oxygen, which in the case of vegetable oils corresponds to their drying power, a classification on the basis of the iodine value would also include the older subdivision into drying and non-drying oils. For these reasons the iodine value has been made one of the chief determinants in the order of enumeration of the natural products dealt with in Vol. II. of this work, and physiological relationship has only been used to a limited extent for grouping together, in subsections, such individuals as seem to possess a uniting bond in that physiological relationship.

Recent researches have established the fact that all vegetable fatty oils and fats are characterised by the occurrence of a **phytosterol** (sitosterol and its congeners), whereas all fatty oils and fats of animal origin contain a **zoosterol** (true cholesterol and its congeners) as the corresponding alcohol. This important distinction naturally leads to a second guiding principle in the subdivision of the glycerides.

Arranging, then, the fatty oils and solid fats according to these two principles, we obtain the following subdivision :—

I. Liquid Fats or Fatty Oils

A. Vegetable oils.
    1. Drying oils.
    2. Semi-drying oils.
    3. Non-drying oils.

B. Animal oils.
    1. Marine animal oils.
        (*a*) Fish oils.
        (*b*) Liver oils.
        (*c*) Blubber oils.
    2. Terrestrial animal oils.

II. Solid Fats

A. Vegetable fats.[1]

B. Animal fats.
    1. Body fats.
        (*a*) Drying fats.
        (*b*) Semi-drying fats.
        (*c*) Non-drying fats.[2]
    2. Milk fats.

In the classification of waxes we can, in our present state of knowledge, adopt the iodine value only as a basis for subdivision, as it is not yet possible to establish a distinction, based on chemical properties, between vegetable and animal waxes. Although a phytosterol has been shown to occur in flax wax, and cholesterol (in association with isocholesterol) in wool wax, definite proof is still wanting that vegetable and animal waxes can be differentiated in a similar manner as in the case of vegetable and animal fats, by the presence or absence of these two alcohols. However, for the sake of uniformity, it may be convenient to carry through the subdivision on the same lines as have been adopted above for fatty oils and fats. We arrive, therefore, at the following classification :—

---

[1] For further subdivision cp. Vol. II. "Vegetable Fats."

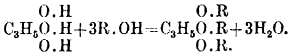
[2] For further subdivision cp. Vol. II. "Animal Fats."

I. Liquid Waxes.	II. Solid Waxes.
	A. Vegetable waxes.
	B. Animal waxes.

I. Fats (Liquid Fats or Fatty Oils, and Solid Fats)

1. Chemical Constitution of Fats—Preparation and Properties of Pure Glycerides

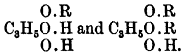
Fats are the product of the combination of glycerol and fatty acids. Glycerol being a trihydric alcohol, and consequently deporting itself like a trihydric base, is able to combine with three radicles of fatty acids, as is expressed by the following equation, in which R represents the acid radicle of any fatty acid :—



$$C_3H_5\begin{matrix}O.H\\O.H\\O.H\end{matrix}+3R.OH=C_3H_5\begin{matrix}O.R\\O.R\\O.R.\end{matrix}+3H_2O.$$

The resulting compounds are called "triglycerides" or "neutral glycyl esters," and they may be compared to neutral salts; therefore the triglycerides are also called *neutral fats*, and the nomenclature used for salts has been adopted for them by some authors. Thus we speak of glyceryl stearate or stearic glyceride, etc. This constitution of fats has been established by the classic researches of *Chevreul* (*Recherches chimiques sur les corps gras d'origine animale*, Paris, 1815–1823. Reprinted 1889), *Berthelot* (cp. *Chimie organique fondée sur la synthèse*, Paris, 1860), and *Wurtz*.

Adopting this constitution of neutral fats, theory predicts the possible existence of monoglycerides and diglycerides corresponding to the formulæ



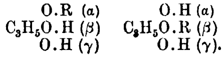
$$C_3H_5\begin{matrix}O.R\\O.H\\O.H\end{matrix}\text{ and }C_3H_5\begin{matrix}O.R\\O.R\\O.H.\end{matrix}$$

Whilst *Chevreul* had compared the glycerides to compound ethers (esters), *Berthelot* amplified *Chevreul's* view by demonstrating that glycerol stood in the same relationship to ethyl alcohol as nitric acid does to orthophosphoric acid. Curiously enough, *Berthelot* compared the monoglycerides, diglycerides, and triglycerides to ortho-, pyro-, and metaphosphates, and it was *Wurtz* who showed that this was inconsistent with the facts discovered by *Berthelot* himself, and thus gave the final explanation which still holds good (cp. Wurtz, *History of Chemical Theory*, p. 139).

In nature apparently only the triglycerides occur; the monoglycerides and diglycerides are, as a rule, not met with in freshly prepared fats. True, *Reimer and Will*[1] found in crude rape oil the diglyceride of erucic acid, $C_3H_5(O.C_{22}H_{41}O)_2(OH)$, but this exception to the general rule is only an apparent one, as the rape oil in question had become hydrolysed with formation of free erucic acid, whilst dierucin separated as a solid mass (see p. 43).

Monoglycerides

Monoglycerides have the general formula $C_3H_5.OR.(OH)_2$. According to the position which the fatty acid radicle occupies in the molecule, two isomeric monoglycerides can exist, as is explained by the following formulæ, in which R denotes the fatty acid radicle:—



$$\begin{matrix} & O.R\ (\alpha) \\ C_3H_5 & O.H\ (\beta) \\ & O.H\ (\gamma) \end{matrix} \qquad \begin{matrix} & O.H\ (\alpha) \\ C_3H_5 & O.R\ (\beta) \\ & O.H\ (\gamma). \end{matrix}$$

It will, of course, be seen, that the (α) and (γ) positions are identical. Compounds corresponding to the first formula will be denoted as α-monoglycerides; they contain an asymmetric carbon atom, and may therefore represent racemic compounds. Monoglycerides corresponding to the second (symmetrical) formula would then appropriately be termed β-monoglycerides. The melting points of the β-monoglyceride are higher than those of the α-isomerides.[2]

Monoglycerides are obtained synthetically by the following general methods. *Berthelot's*[3] classic method consists in heating together fatty acids with an excess of glycerol in a sealed tube. Inasmuch as it is difficult to control the reaction in such a manner that only a monoglyceride (without any diglyceride) be formed, *Romburg*,[4] *Guth*,[5] and *Krafft*[6] mixed equivalent quantities of monochlorohydrin (or bromohydrin) with the finely powdered sodium salt of the fatty acid, and heated the mixture. The sodium chloride formed separates at the bottom of the vessel. The glyceride is then extracted with ether, and filtered over charcoal.

Grün[7] prefers to start (in the case of β-monolaurin) from the more readily obtainable α-γ-dichlorohydrin (1,3 dichloropropanol – 2) which can be converted quantitatively into a dichloro-ester (*e.g.* in the case of lauric acid into β-lauro-α-γ-dichlorohydrin). In order to replace the chlorine atoms by hydroxyl groups, the chloro-compounds are treated with silver nitrite, whereby labile nitrites are formed having the formula $CH_2.O.NO - CH.OR - CH_2.O.NO$. These nitrites are hydrolysed by traces of acids or even by water, and thereby converted into the corresponding hydroxylated compounds, which are the desired β-monoglycerides.

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[1] *Berichte*, 1886, 3320; cp. also Vol. II. Chap. XIV. "Rape Oil."

[2] H. Weyrauch, *Inaug. Dissert.*, Zürich, 1911, p. 17.

[3] *Chimie organique fondée sur la synthèse*, Paris, 1860, vol. ii.

[4] *Rec. d. trav. chim. Pays-Bas*, 1882, 186.

[5] *Zeit. f. Biologie*, 1903, 44, 78.

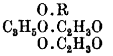
[6] *Berichte*, 1903, 4343.

[7] *Berichte*, 1910, 1288.

According to *B. W. van Eldik Thieme*[1] the foregoing methods do not yield pure products. At any rate in the case of lauric acid he showed that the glycerides prepared by *Grün* and his collaborators (see p. 75) represent mixtures of monoglycerides and diglycerides, inasmuch as by the action of the OH group of the chlorohydrins on the laurates free alkali is formed, whereby partial saponification of the halogenated hydrins takes place. The different melting points recorded in the literature of this subject by the several investigators (see below) thus find a ready explanation. *Van Eldik Thieme* states, however, that pure monolaurins are obtained by using iodohydrins in *Grün's* silver nitrite method.

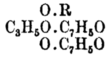
The "biochemical" synthesis (of monoolein) by means of pancreas ferment (*Pottevin*[2]) has no practical importance, but it should be mentioned here, since the action of the ferment appears to exhibit the same catalytic nature[3] as the *Twitchell* reagent (Chap. II. p. 86) possesses. If the latter reagent be added to a mixture of glycerol and fatty acids, glycerol being in excess, and care be taken to remove the water as it is formed, monoglycerides (together with diglycerides) are obtained.[4]

On boiling monoglycerides with acetic anhydride, a mixed triglyceride (see p. 30) of the formula



$$C_3H_5\begin{array}{l}O.R\\ O.C_2H_3O\\ O.C_2H_3O\end{array}$$

is obtained. Similarly, on heating with benzoyl chloride (in the presence of caustic soda), a triglyceride of the formula



$$C_3H_5\begin{array}{l}O.R\\ O.C_7H_5O\\ O.C_7H_5O\end{array}$$

can be prepared.[5]

The following monoglycerides have been obtained hitherto:—

(*a*) *Monoglycerides of Saturated Fatty Acids*

α-*Monoformin*, $C_3H_5(O.CHO)(OH)(OH)$, is obtained by heating monochlorohydrin with sodium formate to 160° C. It is also formed when oxalic acid is heated together with glycerol to 190° C. Monoformin boils in *vacuo* at 165° C.

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[1] *Journ. f. prakt. Chem.*, 1912 (85), 284.

[2] *Compt. rend.*, 1904 (138), 378. Cp. also α-monobutyrin (p. 8).

[3] Lewkowitsch, *Jahrbuch der Chemie*, 1907, xvii. 407.

[4] *Journ. Amer. Chem. Soc.*, 1907, 566. French patent 371,689 (1907).

[5] Quensell (*Inaug. Dissert.*, Berlin, 1909, p. 18) states that the diglycerides of stearolic and behenolic acids could not be converted into the mixed triglycerides by boiling with acetic anhydride; the corresponding monoglycerides assimilated one acetyl group only, forming mixed diglycerides, see p. 17. The same phenomenon was observed in the case of the monoglyceride of ricinstearolic acid, which assimilated (in addition to one acetyl group taken up by the OH group in the molecule of the ricinstearolic acid) one acetyl group only, thus leading to a mixed diglyceride, instead of the triglyceride that would be expected.

α-Monoacetin,[1] $C_3H_5(O\,.\,C_2H_3O)(OH)(OH)$, is obtained (together with diacetin and triacetin) on heating[2] anhydrous glycerin with glacial acetic acid. It is a thick liquid, easily soluble in water and in alcohol, very sparingly soluble in ether, and almost insoluble in benzene. Monoacetin is very hygroscopic. Its specific gravity is 1·2212 at 15° C. (water at 15° C. = 1); it boils unchanged at 130°-132° C. under a pressure of 2-3 mm. At higher pressures it suffers decomposition.

α-Monobutyrin,[3] $C_3H_5(O\,.\,C_4H_7O)(OH)(OH)$, was obtained by *Hanriot* by allowing lipase to act on a mixture of glycerin and butyric acid. It is also formed on heating together equivalent proportions of sodium butyrate and α-monochlorohydrin. It is an oily, colourless liquid of the specific gravity 1·008 at 17° C., boiling under the ordinary pressure at 269°-271° C., and under a pressure of 16 mm. at 160°-163° C. In the butyro-refractometer it indicates 26 " degrees " at 40° C. Monobutyrin is less soluble in water than is monoacetin ; 8 volumes of monobutyrin are miscible with 3 volumes of water ; with 5 or more volumes of water an emulsion is formed.

Monovalerin, $C_3H_5(O\,.\,C_5H_9O)(OH)(OH)$, is obtained by heating valeric acid with glycerol to 200° C. It is an oily liquid of the specific gravity 1·000 at 16° C. One volume of monovalerin forms a clear liquid with half a volume of water, but on adding another half volume or more of water, the monoglyceride is precipitated.

α-Monolaurin, $C_3H_5(O\,.\,C_{12}H_{23}O)(OH)(OH)$, prepared by *Krafft*,[4] from α-monochlorohydrin and potassium laurate, boils *in vacuo* at 142° C. and melts at 59° C.

The α-monolaurin obtained by *Grün's* method from α-laurodi-chlorohydrin melted at 52° C.[5] *B. W. van Eldik Thieme* gives for a pure α-monolaurin the melting point 58·9° C. The α-monolaurin cannot be converted into its phenylurethane by means of phenylisocyanate (difference from β-monolaurin, *Grün*[6]).

β-Monolaurin, $C_3H_5(OH)\,.\,(O\,.\,C_{12}H_{23}O)\,.\,(OH)$, obtained from β-lauro-α-γ-dichlorohydrin by means of silver nitrite, crystallises from ether, petroleum ether, and carbon bisulphide in white silky needles, conglutinating at 58° C. and melting at 61° C. On prolonged keeping the melting point falls to 57·5° C. (*Grün*[7]). *Van Eldik Thieme* gives the melting point 60·5° C.

α-Monomyristin, $C_3H_5(O\,.\,C_{14}H_{27}O)(OH)(OH)$, prepared from α-monochlorohydrin and potassium myristate, boils *in vacuo* at 162° C., and melts at about 68° C. (*Krafft*[8]).

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[1] Geitel, *Journ. f. prakt. Chem.*, 1897 (55), 422, 425.

[2] The immediate formation of monoacetin in the preparation of plastic masses from caseïn, glycerol, and acetic acid was observed by Guédras (*Chem. Zeit.*, 1905, 533).

[3] α-Monoisobutyrin boils at 264°-266° C. under ordinary pressure ; at 158°-161° C. under 16 mm. pressure. In the butyro-refractometer it indicates 21·2 "degrees" at 40° C.

[4] Grün and Skopnik, *Berichte*, 1909, 3755.

[5] *Journ. f. prakt. Chem.*, 1912 (85), 292.

[6] Grün and Skopnik, *Berichte*, 1910, 1290.

[7] *Ibid.*, 1910, 1288.

[8] *Berichte*, 1903, 4343 ; cp. also Grün and Schreyer, *Berichte*, 1912, 3424.

β-Monomyristin, $C_3H_5(OH)(O.C_{14}H_{27}O)(OH)$, obtained from β-myristo-α-γ-dichlorohydrin, melts at 69° C.; it is easily soluble in chloroform, and ether, less readily soluble in alcohol, petroleum ether, and carbon bisulphide (*Weyrauch*[1]).

α-Monopalmitin, $C_3H_5(O.C_{16}H_{31}O)(OH)(OH)$, prepared by *Krafft*[2] from α-monochlorohydrin and potassium palmitate, melted at 72° C.[3] One hundred parts of absolute alcohol dissolve 5·306 parts at 22·5° C. The refraction in *Zeiss*' butyro-refractometer was 25·3 " degrees " at 75° C.

β-Monopalmitin, $C_3H_5(OH)(O.C_{16}H_{31}O)(OH)$, obtained from β-palmito-α-γ-dichlorohydrin, forms white crystalline leaflets, melting at 74° C. After keeping for several months the melting point fell to 69·5° C. (*Grün*[4]).

α-Monostearin, $C_3H_5(O.C_{18}H_{35}O)(OH)(OH)$, obtained from α-monochlorohydrin and potassium stearate, melts at 73° C. (*Guth*); 78° C. (*Krafft*), and crystallises in microscopic needles. It dissolves easily in either hot alcohol or hot ether, but only sparingly in cold ether. It distils unchanged *in vacuo*. The butyro-refractometer index is 28·8 " degrees " at 75° C.[5]

Monoarachin, $C_3H_5(O.C_{20}H_{39}O)(OH)(OH)$, is nearly insoluble in cold ether.

Monocerotin, $C_3H_5(O.C_{26}H_{51}O)(OH)(OH)$, forms long, fine needles, melting at 78·8° C. (*Marie*).[6]

Monomelissin, $C_3H_5(O.C_{30}H_{59}O)(OH)(OH)$, melts at 91·5°-92° C.

(*b*) *Monoglycerides of Unsaturated Fatty Acids*

α-Monoolein, $C_3H_5(O.C_{18}H_{33}O)(OH)(OH)$, is a yellowish liquid of the specific gravity 0·947 at 21° C. (*Berthelot*), solidifying at 0° C. to a white mass; on standing it solidifies slowly at the ordinary temperature (from 15° to 20° C.). *Krafft*[2] obtained from α-monochlorohydrin and potassium oleate a monoolein melting at 35° C., and decomposing on being distilled *in vacuo*. Its refraction in the butyro-refractometer is 60·1 " degrees " at 40° C. The biochemical synthesis of monoolein by *Pottevin* has been already referred to (p. 7). Stereoisomerides of α-monoolein, such as α-monoelaïdin and α-monoisoolein, have not yet been prepared.

If the acid radicle contained in an unsaturated monoglyceride were optically active (*e.g.* if derived from ricinoleic, chaulmoogric, or hydnocarpic acid), the monoglyceride would also exhibit optical activity. An α-monoglyceride containing such an optically active radicle would still represent a racemic compound.

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[1] Cp. also *Berichte*, 1912, 3424.

[2] *Berichte*, 1903, 4343; cp. also Grün and Schreyer, *Berichte*, 1912, 3424.

[3] The melting points 53° C. and 65° C. found by Chittenden and Smith (*Amer. Chem. Journ.* (6), 225) for two monopalmitins undoubtedly refer to mixtures.

[4] *Berichte*, 1910, 1288.

[5] *β-Monostearin*, $C_3H_5(OH)(O.C_{18}H_{35}O)(OH)$, has not been identified with certainty (Grün and Theimer, *Berichte*, 1907, 1792), although Weyrauch (*Inaug. Dissert.*, Zürich, 1911, p. 17) gives for this substance the melting point 80° C.

[6] *Ann. de Chim. et de Phys.* 7, 202.

The following unsaturated monoglycerides have been prepared from fatty acids, not found hitherto in nature.

α-Monostearolin, $C_3H_5(O . C_{18}H_{31}O)(OH)(OH)$, synthesised from glycerol and stearolic acid (*Quensell*[1]), as also from α-monochlorohydrin and sodium stearolate, crystallises from alcohol in white leaflets, melting at 40·5° C., dissolves sparingly in cold alcohol, more readily in warm alcohol, and is easily soluble in chloroform, ether, benzene, and petroleum ether. The *dichloro-addition* product, $C_{21}H_{38}O_4Cl_2$, is obtained as an oily product by allowing equal molecules of α-monostearolin and chlorine to react in a solution of chloroform. The *dibromo-addition* product, $C_{21}H_{38}O_4Br_2$, is obtained by allowing one molecule of bromine to act on one molecule of α-monostearolin in a solution of carbon bisulphide, using metallic iron or ferric chloride as a catalyst. The *diiodo derivative*, $C_{21}H_{38}O_4I_2$, is obtained by allowing iodine to act on α-monostearolin in a solution of carbon bisulphide, in the presence of ferrous iodide and aluminium iodide (which act as catalysts). Even in the presence of the latter the complete absorption of one molecule of iodine requires four to five days, and takes place only on exposure to daylight. The crystals (from alcohol) melt at 33° C.

The *tetrabromo derivative*, $C_{18}H_{38}O_4Br_4$, is obtained with some difficulty by allowing two molecules of bromine (using an excess of 10 per cent) to act on α-monostearolic acid for one week, the solution being exposed at the same time to daylight.[2]

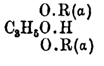
α-Monobehenolin, $C_3H_5(O . C_{22}H_{39}O)(OH)(OH)$, obtained by heating α-monochlorohydrin with sodium behenolate to 160° C., crystallises from alcohol in white leaflets melting at 50·5° C. (*Quensell*[3]). The *dibromo derivative*, $C_{25}H_{46}O_4Br_2$, is obtained by allowing bromine to act on α-monobehenolin in a solution of carbon bisulphide, metallic iron being used as a catalyst.

The *diiodo derivative* is obtained with great difficulty, the reaction becoming complete only after prolonged (over one week) exposure to sunlight.

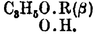
Diglycerides

Diglycerides have the general formula $C_3H_5(OR)_2(OH)$.

Theoretically, two isomeric diglycerides containing *the same fatty acid radicle* can exist, as is indicated by the following two formulæ, in which R denotes the fatty acid radicle :—



$$\begin{matrix} & O.R(\alpha) \\ C_3H_5 & O.H \\ & O.R(\alpha) \end{matrix}$$



$$\begin{matrix} & O.R(\alpha) \\ C_3H_5 & O.R(\beta) \\ & O.H. \end{matrix}$$

Diglycerides of this composition may be termed " simple diglycerides."

The compounds conforming to the first formula will be denoted α-α- (or symmetric) glycerides; they are prepared from α-dichlorohydrin and the salts of fatty acids. The compounds corresponding to the latter formula will be termed α-β- (or unsymmetric) glycerides;

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[1] *Berichte*, 1909, 2441.

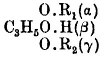
[2] The acetyl and benzoyl derivatives have been referred to in footnote, p. 7.

[3] *Berichte*, 1909, 2445.

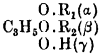
they are prepared in a corresponding manner from β-dibromohydrin. α-β-glycerides contain an asymmetric carbon atom; hence the synthetically prepared α-β-diglycerides are likely to represent racemic compounds.[1] If one or both of the acid radicles were optically active (*e.g.* if derived from ricinoleic, chaulmoogric, or hydnocarpic acid), the diglycerides would be optically active *on that account alone.*

A differentiation between α-α- and α-β-diglycerides might perhaps be based on their different behaviour to thionylchloride with which the α-β-diglycerides react very easily, to form hydrochloric esters of the diglycerides (*i.e.* mixed triglycerides containing Cl in place of one OH group), whereas the α-α-diglycerides react very slowly and incompletely. The mixture of the corresponding mixed triglycerides can be readily separated by means of solvents (*Corelli*).

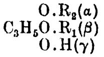
If the *two fatty acid radicles are different,* the existence of diglycerides having the following formulæ is theoretically possible :—



$$\mathrm{C_3H_5}\begin{array}{l}\mathrm{O.R_1}(\alpha)\\ \mathrm{O.H}(\beta)\\ \mathrm{O.R_2}(\gamma)\end{array}$$



$$\mathrm{C_3H_5}\begin{array}{l}\mathrm{O.R_1}(\alpha)\\ \mathrm{O.R_2}(\beta)\\ \mathrm{O.H}(\gamma)\end{array}$$



$$\mathrm{C_3H_5}\begin{array}{l}\mathrm{O.R_2}(\alpha)\\ \mathrm{O.R_1}(\beta)\\ \mathrm{O.H}(\gamma)\end{array}$$

These diglycerides may be termed "mixed diglycerides." As they all contain an asymmetric carbon atom they may represent racemic compounds. If one or both acid radicles be derived from optically active fatty acids, the diglycerides containing them will exhibit optical activity.

Diglycerides are prepared synthetically by the same methods[2] which are employed in the preparation of monoglycerides, with the obvious modifications that a larger proportion of fatty acids must be employed (in *Berthelot's* and *Twitchell's* methods), and that instead of monochlorohydrin (or monobromohydrin), dichlorohydrin (or dibromohydrin) must be used. *Grün*[3] stated that by treating a solution of higher fatty acids in concentrated sulphuric acid (one part of fatty acids in 1·5 parts of sulphuric acid) with glyceroldisulphuric acid (see Chap. III. p. 255), at a temperature of 70° C. for three hours, diglycerides are formed exclusively (neither triglycerides nor monoglycerides having been found in the product of the reaction). The lower the molecular weight of the fatty acid employed, the smaller was the yield of diglyceride. This is explained by *Grün and Schacht*[4] by their observation that the once formed diglycerides combined with free fatty acids to form an addition product. Thus, on allowing myristic acid to react with glyceroldisulphuric acid, the addition compound of the formula $C_3H_5(OH)(OC_{14}H_{27}O)_2 + 2C_{14}H_{28}O_2$ could be isolated. *B. W. van Eldik Thieme*[5] disputed the correctness of *Grün's* statement, and showed, in conformity with the theoretical postulate that mono-, di-, and tri-glycerides should be obtained, that triglycerides are indeed formed, and that subsequently, by the hydrolysing action of water, both diglyceride and monoglyceride are obtained. It would thus appear that under the conditions which *Grün and Schacht* maintained during their experiments the sulphuric acid contained sufficient water to convert triglyceride into diglyceride.

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[1] Experiments made by Corelli to resolve the sulphuric ester of α-β-diglyceride into optically active isomerides by means of their brucine salts did not lead to positive results (*Inaug. Dissert.*, Zürich, 1909).

[2] Cp. also German patent 189,839 (Ulzer, Batik, and Sommer).

[3] *Berichte,* 1905, 2284.

[4] *Ibid.*, 1907, 1778.

[5] *Proceed. K. Akad. d. Wetensch.*, Amsterdam, 1908, 855.

In a more recent publication *B. W. van Eldik Thieme*[1] adduces further proof for the correctness of his views. It is therefore somewhat surprising that *Grün and Corelli* in subsequent publications[2] persist in ignoring the serious objections raised by *van Eldik Thieme.*

On heating diglycerides with acetic anhydride, " mixed triglycerides " of the formulæ

$$C_3H_5(OR)(O.C_2H_3O)(OR) \text{ and } C_3H_5(O.R_1)(O.R_2)(O.C_2H_3O)$$

are obtained. Corresponding " mixed triglycerides " are formed by heating diglycerides with benzoyl chloride.

Simple Diglycerides

(*a*) *Diglycerides of Saturated Fatty Acids*

Diformin, $C_3H_5(O.CHO)_2(OH)$, is obtained as an intermediate product in the preparation of formic acid from oxalic acid and glycerol. On a commercial scale it is prepared by heating 10 parts of pure formic acid with 4 parts of 95 per cent glycerin to 140° C., when dilute formic acid distils over and diformin remains behind.[3] Specific gravity = 1·304 at 15° C. Diformin boils under a pressure of 20-30 mm. at 163°-166° C.

Diacetin, $C_3H_5(O.C_2H_3O)_2(OH)$, is formed, together with monoacetin and triacetin, on heating anhydrous glycerol with glacial acetic acid. It is also obtained by heating glyceroldisulphuric acid and glacial acetic acid for three hours to 70° C. (*Custodis*[4]). Under 40 mm. pressure it boils at 175°-176° C. without undergoing decomposition. Its specific gravity is 1·1769-1·1788 at 15° C. (water at 15° = 1). It is easily soluble in water and in alcohol, less readily so in ether, and with more difficulty still in benzene. Diacetin is a commercial product, and has been used latterly as an adulterant of essential oils.[5]

a-a-Dibutyrin,[6] $C_3H_5(O.C_4H_7O)(OH)(O.C_4H_7O)$, has a specific gravity of 1·083 at 17° C. (*Berthelot*). It boils under a pressure of 19 mm. at 173°-176° C., and under atmospheric pressure at 279°-282° C. The refraction in the butyro-refractometer is 14 " degrees " at 40° C.

a-β-Dibutyrin,[7] $C_3H_5(O.C_4H_7O)(O.C_4H_7O)(OH)$, boils under a pressure of 19 mm. at 166°-168° C., and under atmospheric pressure at 273°-275° C. Its refraction in the butyro-refractometer is 18 "degrees" at 40° C.

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[1] *Journ. f. prakt. Chem.*, 1912 (85), 284.

[2] *Zeits. f. angew. Chem.*, 1912, 665 ; 947.

[3] S. von Kapff, United States patent 901,298.

[4] *Inaug. Dissertation,* Zürich, 1909.

[5] *Journ. Soc. Chem. Ind.*, 1903, 570 ; cp. Vol. III. Chap. XV.

[6] a-a-Diisobutyrin boils under ordinary pressure at 272°-275° C., under 22 mm. pressure at 164°-167° C. In the butyro-refractometer it indicates 10·3 "degrees" at 40° C.

[7] a-β-Diisobutyrin boils under ordinary pressure at 269°-272° C., under 20 mm. pressure at 159°-162° C. In the butyro-refractometer it indicates 11·5 "degrees" at 40° C.

Divalerin, $C_3H_5(O.C_5H_9O)_2(OH)$, has the specific gravity 1·059 at 16° C.

α-α-Dilaurin, $C_3H_5(O.C_{12}H_{23}O)(OH)(O.C_{12}H_{23}O)$, is obtained by the action of glyceroldisulphuric acid on lauric acid (yield 35 per cent) as also from α-α-dichlorohydrin and potassium laurate (yield 81 per cent). The product prepared by the first method is liquid, and gives only with difficulty a small quantity of crystals melting after recrystallisation at 57° C., whereas the α-α-dilaurin obtained by the second method yields more readily crystals melting at 55° C.[1] (cp. below, "Double Melting Point," p. 21).

B. W. van Eldik Thieme (*Journ. f. prakt. Chem.*, 1912 (85), 295), however, found that in this reaction α-β-dilaurin, trilaurin, and most likely a little α-α-dilaurin are formed. The true α-α-dilaurin is a liquid.

By varying the temperature at which potassium laurate and α-α-dichlorohydrin are allowed to act on each other, the yield of solid α-α-dilaurin varies; thus, the higher the temperature the greater is the proportion of liquid α-α-dilaurin. The solid α-α-dilaurin is separated from the liquid α-α-dilaurin by admixing with the crude product of the reaction some alcohol and filtering in the cold on a vacuum filter, whereby the bulk of the liquid together with small quantities of solid α-α-dilaurin pass through the filtering medium. Heating to 150° C. did not convert the solid α-α-dilaurin into the liquid modification.

The solid α-α-dilaurin does not form an addition compound with lauric acid (see α-α-dimyristin). The crystals which separate from the liquid α-α-dilaurin (obtained from glyceroldisulphuric acid and lauric acid) melt at 40° C., whereas the solid α-α-dilaurin obtained from potassium laurate and α-α-dichlorohydrin melt at 57° C. After standing for several months, both solid modifications of α-α-dilaurin melt at 45° C., and even a mixture of the two solid α-α-dilaurins melts at the same temperature of 45° C.

The liquid dilaurin could not be converted into a solid modification by heating to 150° C. for three hours; in contradistinction to the behaviour of the solid α-α-dilaurin, hydrolysis of the diglyceride took place to a considerable extent.

The liquid α-α-dilaurin yields in the molecular weight-determination by the cryoscopic method (in benzene) only half the theoretical value, a phenomenon which has hitherto not found an explanation (cp. trilaurin, p. 26). Both solid α-α-dilaurins give, when examined by the same method, values which are very little higher than those demanded by theory (dilaurin of melting point 40° C. gave 517·4; α-α-dilaurin of melting point 57° C. gave 511·3; theory: 456·42) (*Custodis*).

α-α-dilaurin is soluble in alcohol, ether, and chloroform.

α-β-Dilaurin, $C_3H_5(O.C_{12}H_{23}O)(O.C_{12}H_{23}O)(OH)$, is prepared by heating α-β-dibromohydrin with potassium laurate (*Reinhardt*[2]).

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[1] Grün and Schacht, *Berichte*, 1907, 1788. Custodis, *Inaug. Dissert.*, Zürich, 1909.

[2] *Inaug. Dissert.*, Zürich, 1909.

It crystallises from its hot petroleum ether solution (after adding cold petroleum ether) in crystals, softening at 50° C. and melting at 56° C., 56·3° C. (*van Eldik Thieme*). This dilaurin is soluble in 95 per cent alcohol, but insoluble in 60 per cent alcohol even on warming.

α-α-Dimyristin, $C_3H_5(O.C_{14}H_{27}O)(OH)(O.C_{14}H_{27}O)$, is obtained from glyceroldisulphuric[1] acid and myristic acid; the yield is only 40 to 46 per cent; the main product is an addition compound of the formula $C_3H_5(O.C_{14}H_{27}O)_2(OH) + 2C_{14}H_{28}O_2$ forming small white crystals melting at 53·5° C. (from alcohol or ether) or 55° C. (from amyl alcohol). This α-α-dimyristin forms white crystals sparingly soluble in petroleum ether, melting at 63° C. (from alcohol or ether), 65° C. (from amyl alcohol). After prolonged keeping the melting point drops to 62·5° C.

The α-α-dimyristin obtained from α-α-dichlorohydrin and potassium myristate forms white crystals, melting at 55° C. and 61° C. and after solidification at 61° C. After keeping for several months, the crystals melt at 59° C., and show the same melting point even after solidification.[2]

α-β-Dimyristin,[2] $C_3H_5(O.C_{14}H_{27}O)(O.C_{14}H_{27}O)(OH)$, prepared from α-chlorodimyristin by heating with silver nitrite and saponifying the nitrous ester, melts at 64·5° C., and exhibits the same melting point after solidification. After several months' keeping it melted at 62·5° C., and then shortly after solidification at 50° C., and after a further twenty-four hours at 60° C.

α-α-Dipalmitin, $C_3H_5(O.C_{16}H_{31}O)(OH)(O.C_{16}H_{31}O)$. The dipalmitin of the melting point 59° C., obtained by *Berthelot* on heating glycerol and palmitic acid, as also the dipalmitin of the melting point 61° C., prepared by *Chittenden and Smith*, are most likely identical with the product obtained by *Guth* on heating two molecules of sodium palmitate with one molecule of α-α-dichlorohydrin. Provided no molecular rearrangement takes place on heating, the constitution of this compound must be that of an α-α-diglyceride. This view is confirmed by *Grün's*[3] synthesis of the same diglyceride from palmitic acid and glyceroldisulphuric acid. It melts at 69° C. (*Guth*), 70° C. (*Grün*); on keeping for a prolonged time the melting point rises to 73°-74° C. (*Corelli*[4]). In the butyro-refractometer it indicates 23·8 "degrees" at 75 C.

α-β-Dipalmitin, $C_3H_5(O.C_{16}H_{31}O)(O.C_{16}H_{31}O)(OH)$, obtained from sodium palmitate and α-β-dibromohydrin, melts at 67° C. (*Guth*); in the butyro-refractometer it indicates 21·8 "degrees" at 75° C.

α-α-Distearin, $C_3H_5(O.C_{18}H_{35}O)(OH)(O.C_{18}H_{35}O)$. The product obtained by *Berthelot* (1) on heating 1 part of α-monostearin with 3 parts of stearic acid to 260° C. for three hours; (2) on heating stearin with an excess of glycerol to 220° C. for twenty-two hours; (3) on heating equal parts of glycerol and stearic acid to 160° C. for fourteen hours (yielding a product of melting point 58° C.), as also the distearin of the melting point 76·5° C. obtained by *Hundeshagen*,[1] is very likely the α-α-compound. *Guth* synthesised this α-α-distearin by heating one molecule of α-α-dichlorohydrin with two molecules of sodium stearate in a sealed tube to 140°-150° C. for six to eight hours. This distearin crystallises from petroleum ether in rhombic plates, melting at 72·5° C. In the butyro-refractometer it indicates 25·3 "degrees" at 75° C. *Bömer*[2] in a more recent preparation of this glyceride, following *Guth's* method, found that considerable amounts of tristearin are formed simultaneously, and that consequently the statements of previous observers refer to an impure product. *Bömer* finds that a carefully prepared specimen of α-α-distearin, freed from tristearin, melts at 76·5° C.

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[1] Grün and Schacht, *Berichte*, 1907, 1785.

[2] Grün and Theimer, *Berichte*, 1907, 1797.

[3] *Berichte*, 1905, 2285; cp., however, van Eldik Thieme's strictures, p. 75.

[4] *Inaug. Dissert.*, Zürich, 1909.

The α-α-distearin obtained from stearic acid and glyceroldisulphuric acid (yield 76 per cent; *Grün*[3]) conglutinates at 58° C., and melts at 76° C.; after several months it melted at 74·5° C. (*Grün and Schacht*[4]).

α-β-Distearin, $C_3H_5(O\,.\,C_{18}H_{35}O)(O\,.\,C_{18}H_{35}O)(OH)$, is obtained from one molecule of α-β-dibromohydrin and two molecules of sodium stearate. It crystallises from petroleum ether in prismatic plates, melting at 74·5° C. The melting point of α-β-distearin obtained from α-chloro-glyceroldisulphuric acid and silver nitrite is 78·2° C., and after several days' standing 77·5° C. (*Grün and Theimer*[5]). In the butyro-refractometer it shows 25 "degrees" at 75° C.

α-α-Diarachin, $C_3H_5(O\,.\,C_{20}H_{39}O)(OH)(O\,.\,C_{20}H_{39}O)$, melts at 75° C. (*Berthelot*; *Grün*); it is almost insoluble in cold ether, but very readily soluble in carbon bisulphide.

Dicerotin, $C_3H_5(O\,.\,C_{26}H_{51}O)_2(OH)$, melts at 79·5° C.; it is almost insoluble in boiling alcohol.

Dimontanin, $C_3H_5(O\,.\,C_{29}H_{57}O)_2(OH)$, is stated to be obtained by heating refined montan wax with glycerin,[6] and is said to melt at 80°-81° C.

Dimelissin, $C_3H_5(O\,.\,C_{30}H_{59}O)_2(OH)$, melts at 90° C.

(*b*) *Diglycerides of Unsaturated Fatty Acids*

α-α-Diolein, $C_3H_5(O\,.\,C_{18}H_{33}O)(OH)(O\,.\,C_{18}H_{33}O)$. The product obtained by *Berthelot* on heating 1 part of α-monoolein with 5 parts of oleic acid to 250° C. for several hours, or on heating olein with glycerol to 200° C. for twenty-two hours, is most likely the α-α-compound. The true α-α-diolein was prepared by *Guth* from α-α-dichlorohydrin and sodium oleate. α-α-diolein differs very little in its physical properties from α-monoolein. Like the latter, it solidifies at 0° C. to a white mass, which is converted into a translucent mass containing white granular particles, on standing a few days at the ordinary temperature. In the butyro-refractometer it indicates 58·8 "degrees" at 40° C.

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[1] *Journ. f. prakt. Chem.* 28, 227.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, xxv. 354.

[3] *Berichte*, 1905, 2284.

[4] *Ibid.*, 1907, 1781.

[5] *Ibid.*, 1907, 1793; cp. also Reinhardt.

[6] Ernst Schliemann's *Export-Ceresin Fabrik.* German patent 244,786.

α-β-Diolein, $C_3H_5(O.C_{18}H_{33}O)(O.C_{18}H_{33}O)(OH)$, prepared from α-β-dibromohydrin and sodium oleate, resembles the α-α-compound in colour, smell, and taste. It also solidifies at 0° C., but differs from the α-α-compound in that it remains liquid at the ordinary temperature, even if allowed to stand for several weeks. In the butyro-refractometer it indicates 56·3 " degrees " at 40° C.

Stereoisomerides of diolein have not been prepared hitherto.

Dierucin, $C_3H_5(O.C_{22}H_{41}O)_2(OH)$, melts at 47° C. It is almost insoluble in ether and in petroleum ether. Its occurrence in old rape oil has been pointed out above (p. 6).

Dibrassidin, $C_3H_5(O.C_{22}H_{41}O)_2(OH)$, melts at 67° C.; it dissolves with difficulty in ether.

α-α-Dilinolin, $C_3H_5(O.C_{18}H_{31}O)(OH)(O.C_{18}H_{31}O)$, prepared from α-α-dichlorohydrin and potassium linolate, is a yellow oil of neutral reaction. Its derivative $C_3H_5(O.C_{18}H_{31}Br_4O)(OH)(O.C_{18}H_{31}Br_4O)$, prepared from dichlorohydrin and potassium tetrabromostearate (from linolic tetrabromide), melts at 71°-72° C., is easily soluble in ether, and more easily soluble in alcohol than α-α-dilinolin (*H. Schoenfeld*[1]).

The following unsaturated diglycerides have been prepared from fatty acids, not found hitherto in nature :—

α-α-Distearolin, $C_3H_5(O.C_{18}H_{31}O)(OH)(O.C_{18}H_{31}O)$, prepared by heating α-α-dichlorohydrin with sodium stearolate at 180° C., crystallises from low boiling petroleum ether in white leaflets, melting at 38° C., and from alcohol in needles melting at 38·5° C. It is sparingly soluble in cold, somewhat more readily soluble in boiling alcohol, and dissolves readily in ether, benzene, petroleum ether, and chloroform (*Quensell*[2]).

α-β-Distearolin, $C_3H_5(O.C_{18}H_{31}O)(O.C_{18}H_{31}O)(OH)$, prepared by heating α-β-dibromohydrin with an excess of sodium stearolate to 175° C., melts at 40° C. (*Quensell*[2]). On heating with acetic anhydride and sodium acetate no assimilation of an acetyl group took place (see footnote p. 7).

α-α-Dibehenolin, $C_3H_5(O.C_{22}H_{39}O)(OH)(O.C_{22}H_{39}O)$, is formed on heating α-α-dichlorohydrin with sodium behenolate to 170° C. The crystals, obtained from petroleum ether, melt at 42° C.; those obtained from alcohol melt at 43° C. (*Quensell*[2]).

The tetrachloro derivative, $C_3H_5(O.C_{22}H_{39}Cl_2O)_2(OH)$, is obtained by the action of chlorine on a solution of α-α-dibehenolin in carbon bisulphide (*Quensell*[2]).

The *tetraiodo derivative*, $C_3H_5(OC_{22}H_{39}I_2O)_2(OH)$, is obtained with the aid of a catalyst (mercury bichloride) from α-α-dibehenolin and iodine in a solution of carbon bisulphide.

α-β-Dibehenolin, $C_3H_5(O.C_{22}H_{39}O)(O.C_{22}H_{39}O)(OH)$, is prepared from α-β-dibromohydrin and sodium behenolate at 180° C. The crystals, obtained from alcohol, melt at 43° C. (*Quensell*[2]). On heating with acetic anhydride and sodium acetate no assimilation of an acetyl group took place (see footnote, p. 7).

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[1] *Inaug. Dissert.*, Zürich, 1912.

[2] *Berichte*, 1909, 2443.

Mixed Diglycerides

(*a*) *Diglycerides of Saturated Acids*

(1) *α-α Compounds*

α-Lauro-α-myristin, $C_3H_5(O.C_{12}H_{23}O)(OH)(O.C_{14}H_{27}O)$, obtained by heating α-lauro-α-monochlorohydrin with potassium myristate to 140° C.,[1] crystallises (from dilute petroleum ether and common ether, cooled below 0° C.) in shining white crystals, melting at 40°-42° C. The solidified mass melts again at 34°-35° C.

α-Lauro-α-stearin, $C_3H_5(O.C_{12}H_{23}O)(OH)(O.C_{18}H_{35}O)$, obtained by heating α-chloro-γ-monostearin (or α-stearo-α-monochlorohydrin) with potassium laurate to 120° C.,[1] crystallises from a cooled mixture of ether and petroleum ether in granular crystals, melting at 52°-53° C. After solidification the mass melts at 45° C.

α-Stearo-α-myristin, $C_3H_5(O.C_{18}H_{35}O)(OH)(O.C_{14}H_{27}O)$, obtained by heating α-stearo-α-monochlorohydrin with potassium myristate,[1] crystallises (from a mixture of ether and petroleum ether) in crystals, softening at 47° C., and melting at 52°-53° C. The solidified mass melts at 44° C.

(2) *α-β Compound*

α-Myristo-β-stearin, $C_3H_5(O.C_{14}H_{27}O)(O.C_{18}H_{35}O)(OH)$, obtained by heating α-myristo-α-monochlorohydrin with stearyl chloride and treating the myristo-stearo-chlorohydrin with silver nitrite, etc., melts at 58° C. (*Grün and Schreyer*[2]).

(*b*) *Diglycerides of Unsaturated Acids*

α-Acetyl-γ-stearolin, $C_3H_5(O.C_2H_3O)(OH)(O.C_{18}H_{31}O)$, obtained on boiling α-monostearolin with acetic anhydride and sodium acetate, forms a viscous oil which solidifies in a freezing mixture. It is noteworthy that a second acetyl group is not assimilated (*Quensell*[3]).

α-Acetyl-γ-acetylricinstearolin, $C_3H_5(O.C_2H_3O)(OH)(O.C_{18}H_{31}[O.C_2H_3O])$, is obtained by boiling α-monoricinstearolin (prepared from sodium ricinstearolate and α-monochlorohydrin) with acetic anhydride. One acetyl group is assimilated by the (OH) group in the ricinstearolic acid radicle, and a second acetyl group by one of the hydroxyl groups of the monoglyceride. A further assimilation of an acetyl group with the formation of a triglyceride could not be effected.

Triglycerides

Theory predicts the existence of two classes of triglycerides, according to whether all three fatty acid radicles in the molecule have the same or a different composition. The former may be termed *simple triglycerides*, whereas the latter are suitably denominated *mixed triglycerides*.

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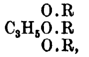
[1] Grün and Skopnik, *Berichte*, 1909, 3757.

[2] *Berichte*, 1912, 3420.

[3] *Inaug. Dissert.*, Berlin, 1909.

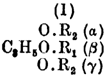
In the former class only one representative can exist for each fatty acid, namely,



$$\begin{array}{l} \qquad O.R \\ C_3H_5O.R \\ \qquad O.R, \end{array}$$

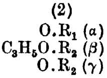
whereas in the second class two isomeric triglycerides may be expected if they contain two different fatty acid radicles, and three isomerides in the case of all three fatty acid radicles being different. This is explained by the following formulæ :—

(1)



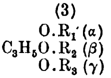
$$\begin{array}{l} \qquad O.R_2\,(\alpha) \\ C_3H_5O.R_1\,(\beta) \\ \qquad O.R_2\,(\gamma) \end{array}$$

(2)



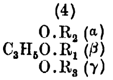
$$\begin{array}{l} \qquad O.R_1\,(\alpha) \\ C_3H_5O.R_2\,(\beta) \\ \qquad O.R_2\,(\gamma) \end{array}$$

(3)



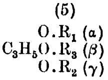
$$\begin{array}{l} \qquad O.R_1'\,(\alpha) \\ C_3H_5O.R_2\,(\beta) \\ \qquad O.R_3\,(\gamma) \end{array}$$

(4)



$$\begin{array}{l} \qquad O.R_2\,(\alpha) \\ C_3H_5O.R_1\,(\beta) \\ \qquad O.R_3\,(\gamma) \end{array}$$

(5)



$$\begin{array}{l} \qquad O.R_1\,(\alpha) \\ C_3H_5O.R_3\,(\beta) \\ \qquad O.R_2\,(\gamma) \end{array}$$

It will be seen that in triglycerides represented by formula (1) the α and γ-positions are identical; glycerides of this constitution might be termed "symmetrical mixed triglycerides," whereas triglycerides represented by formula (2), in which the β and γ positions are different, would consequently be termed "unsymmetrical mixed triglycerides." The same term might also be applied to the mixed triglycerides represented by formulæ (3), (4), and (5).

The number of simple triglycerides is limited by the number of fatty acids (and their isomerides) which occur in nature. Infinitely larger is, however, the number of possible "mixed glycerides." *Berthelot,*[1] as also *Kablukow,*[2] have given formulæ for calculating the possible number mathematically. No useful purpose would be served here by reproducing these formulæ, all the less so because the numbers thus calculated must be increased very considerably by taking into account the variations introduced by the existence of stereo-isomeric compounds —*e.g.*, from elaïdic and brassidic acids—and by the possible existence of optically active compounds, obtainable by the resolution of racemic compounds, as represented by the last four formulæ, into optically active antipodes, and furthermore by those optically active mixed glycerides which owe their optical activity to the asymmetric configuration of the optically active fatty acid radicles themselves.

Until recently most of the natural fats were considered to consist of mixtures of simple triglycerides of the several fatty acids, although *Berthelot*[3] had already pointed out that the complexity of the natural oils and fats might be best explained by the existence of mixed glycerides. In favour of the former assumption it was maintained that on cooling liquid fats, tripalmitin and tristearin separated out either in their pure state or as a mixture. The theoretical postulate, that there should exist mixed glycerides, had up to recently obtained but very slender support from the experiments of *Bell and Lewin* (see Vol. II. Chap. XIV. "Butter Fat"), which led *Bell* to the conjectural statement that in cow butter probably oleopalmito-butyrate, of the formula

$$C_3H_5(O.C_{18}H_{33}O)(O.C_{16}H_{31}O)(O.C_4H_7O),$$

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[1] *Chimie organique fondée sur la synthèse,* 1860, vol. ii. p. 33.

[2] *Chem. Centralbl.,* 1888, i. 73.

[3] *Chimie organique, etc.,* 1860, vol. ii. p. 31.

occurred. Since *Heise*[1] discovered oleodistearin in mkányi fat and in kokum butter, other experimenters have isolated from natural fats a considerable number of mixed triglycerides (see p. 31).

The preparation of pure triglycerides from natural products is a very laborious task, and has not always been accomplished satisfactorily, owing to the great difficulty of separating the various triglycerides. Thus *Duffy*,[2] on recrystallising 2000 grms. of mutton tallow from large quantities of ether, obtained, after thirty-two successive crystallisations, no more than 8 grms. of substance, which even then could not be considered to be pure tristearin. Again *Krafft*[3] showed that whilst in a perfect vacuum trilaurin and trimyristin could be obtained (by fractional distillation) from laurel oil and nutmeg butter respectively, in such a state of purity that after one crystallisation glycerides of normal melting points are obtained, higher triglycerides underwent decomposition, so that, *e.g.*, pure tripalmitin could not be prepared from Japan wax by this method. A more satisfactory, though still extremely laborious, method is afforded by a systematic crystallisation of tallow[4] from ether, followed by recrystallisation from benzene (cp. Chap. XII.). Hence, for the preparation of pure triglycerides in large quantities synthetical methods must be employed.

Pure triglycerides were first obtained by *Berthelot*[5] on heating glycerol with fatty acids. As has been explained already, monoglycerides and diglycerides are formed simultaneously. In order to exclude the formation of these lower glycerides, and with a view to obtaining complete esterification by removing the water as it was formed, *Scheij*[6] heated glycerol with an excess of fatty acid in a slow current of air. In the case of the triglycerides of the fatty acids of low molecular weights, *i.e.* up to acids having ten carbon atoms in their molecule, a small quantity of fatty acids distils over simultaneously with the water, and it is therefore necessary to add, from time to time, a fresh quantity of the fatty acid. In the case of the fatty acids of higher molecular weight, the reaction is complete when water ceases to be evolved. The reaction can be accelerated by adding a small quantity of *Twitchell's* reagent (see Chap. II.).

The pure glycerides may also be prepared by heating together the sodium (or silver) salts of the fatty acids with tribromohydrin (*Guth; Partheil and v. Velsen*[7]).

The property of exhibiting a so-called double melting point has been looked upon as characteristic of pure triglycerides (as also of the natural fats which constitute mixtures thereof). A number of observers (amongst whom should be mentioned *Chevreul*) stated that the triglycerides melt at a certain degree of temperature, then solidify at a higher degree, to melt again on further heating. This curious behaviour was explained by *Duffy*, and after him by *Heintz*, by the assumption that the triglycerides exist in two modifications. In the case of tristearin, for which the two melting points 55° C. and 71° C. had been observed, *Guth*[1] showed later on that well-crystallised tristearin has only one melting point, viz. 71·5° C., and he further pointed out that it exhibits the same melting point even after it has been melted, provided it be kept in the capillary tube for some time after melting. If, however, the tristearin was examined shortly after having been melted in the capillary or if it was introduced into the capillary in a liquid state and was then cooled rapidly, it exhibited two melting points. *Guth* further ascertained that at the lower temperature the substance would only melt completely when the capillary tube was very narrow, and the quantity of the substance very small; on examining a somewhat larger quantity of tristearin in a comparatively wide capillary tube, complete melting did not occur at the lower temperature, the mass becoming only soft and translucent; it then solidified again and finally melted at 71·5° C. to a clear liquid. The different behaviour of the crystalline tristearin on the one hand, and of the once fused tristearin on the other, was explained by *Guth* by the suggestion that the melted (at 55° C.) and rapidly solidified substance had not yet passed into the crystalline state, and behaved in a manner similar to that of under-cooled water (which has remained liquid below 0° C.) or a super-saturated solution of sodium sulphate. If the substance be then shaken or disturbed on raising the temperature, it solidifies again to its original state, the latent heat thus set free sufficing to melt the whole mass, if the quantity be small. If, however, the quantity of substance be large, the heat set free cannot effect complete melting, since the surrounding water still absorbs the liberated heat. *Guth* further showed that crystallised tripalmitin, as also stearodipalmitin and palmitodistearin, have one melting point only, but under conditions similar to those stated above for tristearin, they exhibited two melting points[2] (cp. below).

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[1] *Arbeiten aus d. Kaiserl. Gesundheitsamte*, 1896, xii. 540; xiii. 302.

[2] *Journ. Chem. Soc.*, 1852 (5), 199; cp. Heintz, *Journ. f. prakt. Chem.*, 1855 (66), 49.

[3] *Berichte*, 1903, 4343.

[4] Bömer, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 91; also of lard, *ibid.*, 1913.

[5] *Ann. de Chim. et de Phys.*, 1854 [3], 41, 420.

[6] *Rec. d. trav. chim. Pays-Bas*, 18, 169.

[7] *Archiv d. Pharm.*, 1900 [238], 267.

Grün and Schacht,[3] as also *Bömer*,[4] showed, however, independently of each other, that *Guth's* deductions are open to objections, and that the earlier views of *Duffy* and *Heintz* must be reinstated. *Grün and Schacht* state that the phenomenon of the double melting point must be ascribed to the actual existence of two isomeric modifications. They prepared three mixed glycerides, which were obtained both in an unstable ("labile"), lower melting modification, and in a stable ("stabile"), higher melting modification. The unstable form could be gradually converted into the stable form by inoculating the former with a crystal of the stable modification; it was not, however, possible to effect the reverse change. Nor was it found possible to decide whether the difference between unstable and stable forms may be due to polymerisation, as the determinations of the molecular weight by means of the freezing and boiling point methods did not furnish decisive results. [The actual occurrence of two modifications was still more strikingly demonstrated in the case of α-α-dilaurin (see p. 13) and α-β-γ-laurodimyristin. Curiously enough, the liquid modification of α-α-dilaurin gave only half the theoretical value in the cryoscopic method of determining its molecular weight, a phenomenon which was also observed in the case of liquid trilaurin (*Custodis*[1]).] *Bömer*[2] studied carefully the transformation of the unstable form of glycerides (especially of tristearin) into the stable form, and indicated explicitly the conditions under which the so-called "first melting point" can be observed. (*Bömer* proposes to term the first melting point "transition point.") The stable form is that crystalline form in which glycerides are obtained from solutions. In the case of pure glycerides the "transition point" is almost identical with the solidifying-point of the "crystallised form"; in the case of impure glycerides the "transition point" is lower. This can be verified experimentally by causing the labile form, obtained by rapid cooling of the solidified substance, to pass again into the stable form.[3] This is done by warming the substance about 5° C. above the "transition point" and allowing the temperature to fall again within 5 to 10 minutes to the transition point (cp. Chap. XII.). In some cases, however (mutton tallow), the time of heating must be prolonged. *Bömer* considers that the melting point of glycerides which have been obtained from solutions in the *crystalline* form should be looked upon as the true melting point. (Pure glycerides have one and the same melting point whether they be obtained in the crystalline form from a solution or from the solidified, once melted crystals.) *Guth's* observations on tristearin are therefore readily explained by the fact that the tristearin examined by him was obtained in the *crystalline* state from a solution.

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[1] *Zeits. f. Biologie*, 44, 78; cp. Wimmel, *Zeits. f. analyt. Chem.*, 1868 (vii.), 269, and A. Smits and S. C. Bokhorst, *Proc. k. Acad. v. Wetensch.*, Amsterdam, 1912 (15), 681.

[2] Kreis and Hafner confirmed Guth's observations (*Berichte*, 1893, 1125).

[3] *Berichte*, 1907, 1778; cp. Grün, *Berichte*, 1912, 3692.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 97; 1909, xvii. 362.

In further confirmation it may be mentioned that well-crystallised brassidin shows one melting point only, even after it has been heated to about 40° C. above its melting point.

In the light of *Jaeger's*[4] views, the unstable modification may be looked upon as a case of an anisotropic liquid phase, such as was observed in the case of phytosteryl-n-valerate.[5] The case of α-α-dilaurin occurring in a liquid modification which is gradually converted into one of the two solid modifications of α-α-dilaurin (*Custcdis*[6]) would seem to confirm this. There are, however, some different modifications of glycerides known, the existence of which cannot be explained satisfactorily as yet. Such modifications are those of β-lauro-α-γ-distearin, β-myristo-α-γ-distearin, β-myristo-α-γ-dilaurin, and trinitroglycerin.

The above described phenomena are in conflict with the physical law that melting and solidifying are reciprocal, reversible phenomena which take place at exactly the same temperature. This induced *H. Le Chatelier and Mlle Cavaignac* [1] to study carefully the phenomenon of the so-called double melting point in the case of refined cocoa nut oil and stearin; they conclude from their experiments that the fats do not occupy an exceptional position, and that the above physical law also holds good for them; in other words, that in the case of fats also, melting and solidifying is a reversible process. The fats behave in a peculiar manner only in that respect that the velocity of the change is extremely slow. If the observation of melting and solidifying points be carried out with sufficient slowness, the reversible process takes place within 0·1 to 0·2 of a degree. If, however, it is done rapidly, greater variations occur. (Such greater rapidity is, of course, the usual feature of the laboratory process of determining the melting point of fats.) No fact was observed which leads to the assumption of the existence of several polymorphic varieties, although the possibility of their existence cannot be excluded. In that case, however, the problem would become much more complicated, as the number of phases increases, and no definite temperature can be found before all solid phases less one, have disappeared. The time necessary therefor must be very long, judging from the slowness of crystallisation of one single solid phase. (*H. Le Chatelier and Mlle Cavaignac* compare the slowness of the crystallisation of fats with that of the devitrification of glass.) The ordinary methods of observation of melting and solidifying points are therefore to a large extent influenced by (in other words, are functions of) the rapidity of heating and cooling.

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[1] *Inaug. Dissert.*, Zürich, 1909.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 97; 1909, xvii. 362.

[3] The transition point is therefore that temperature at which the labile form passes into the stable form. Nitroglycerin also appears to occur in an unstable and a stable form (see Chap. III.).

[4] *Rec. d. trav. chim. Pays-Bas*, 1906 [25], 346.

[5] Cp. also Knövenagel's (*Berichte*, 1907, 515) "motoisomerism," and the curious phenomena observed in the case of allo- and iso-cinnamic acids (Biilmann, *Berichte*, 1909, 182, and Liebermann, *ibid.*, 1909, 1028). Cp. also Grün, *Berichte*, 1912, 3692.

[6] *Inaug. Dissert.*, Zürich, 1909; Grün, *Berichte*, 1912, 3692.

Whilst the temperature of the melting point remains approximately constant, and about 1° C. above the point of change of the reversible state (which should correspond with *Bömer's* "transition point"), the temperature of solidification, on the contrary, falls in proportion as the rapidity of cooling increases. The difference between the two temperatures increases, however, and reaches about 5° C. on the average, if the rapidity of cooling and heating varies between 4° C. and 40° C. per hour.

Foreign substances have a decided influence on the melting point, and if they are present, fats exhibit a state of super-fusion.

These views are not in complete agreement with those held by *Bömer*, and it would appear as if the conclusions depend to a great extent on the method employed in carrying out the experiments. As stated above, the melting point and solidifying point of pure glycerides should be identical, yet experiments published recently by *Bömer and Limprich*,[2] and reproduced in the following table, show that the "transition point" of pure glycerides can be observed distinctly, and that the authors find therein fresh support for their view that the glycerides exist in two forms, viz. "stabile" and "labile," as pointed out above. They also observed (thus confirming *Guth*), that pure glycerides require some prolonged warming above the temperature of the "transition point" before the labile form of the glyceride has been converted completely into the "stabile" form. If such prolonged warming has taken place the glycerides no longer show a "transition point," but exhibit melting points which are in full agreement with the melting points obtained for the "stabile" form.

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[1] *Compt. rend.*, 1913 (156), 589.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, xxv. 373.

	Melting Point[1] °C.	"Transition Point" °C.	Solidifying Point[1] °C.	Commenced to solidify at °C.	Melting Point of Glyceride heated above its Transition Point, °C.
Tristearin[2] . . .	73·2	55·5	53·5	58	73·6
β-Palmito-α-γ-distearin[2]	61·5 (64·0)[4]	52·1	49·7	55	63·4
Stearodipalmitin	58·1	(48)	45·9	52	58·5
α-Palmito-β-γ-distearin[3]	68·4	52·2	50·0	55	68·5
Stearodipalmitin[3] .	58·3	48·2	45·9	53	58·8

The following triglycerides have been obtained hitherto in a state of purity :—

Simple Triglycerides

(a) *Simple Triglycerides of Saturated Fatty Acids*

Triformin, Formin, $C_3H_5(O\,.\,CHO)_3$, is obtained from pure diformin (p. 12) by treating it with anhydrous formic acid (*Romburgh*[5]). It can also be isolated from the product obtained in the preparation of diformin. Triformin crystallises in needles melting at 18° C. In its liquid form it has the specific gravity 1·320 at 18° C. and $n_D^{18} = 1{\cdot}4412$; it boils at 163° C. under 38 mm., and at 266° C. under 760 mm. pressure. On distilling triformin, under ordinary pressure very slowly, it is decomposed, with evolution of carbon monoxide and dioxide, into allyl formate, formic acid, and amyl alcohol, which distil over, whereas glycerol remains in the residue. Triformin is hydrolysed slowly by cold water, more rapidly by warm water. With ammonia and amides it yields the corresponding formamide and glycerol.

Triacetin, Acetin, $C_3H_5(O\,.\,C_2H_3O)_3$, is prepared by heating 20 c.c. of glycerol with 10 c.c. of acetic anhydride and 50 grms. of finely powdered hydrogen potassium sulphate. As soon as a violent reaction sets in, 20 c.c. more of acetic anhydride are added and the mixture is boiled for some time. The cooled mass is exhausted by means of ether, when a mixture of triacetin and diacetin is obtained, which can be separated into its components by fractional distillation. Triacetin boils at 172°-172·5° C. under 40 mm. pressure, and at 258°-259° C. under ordinary pressure. Its specific gravity is 1·1603 at 15° C. (water 15° C. = 1). It is miscible with alcohol, ether, chloroform, and benzene; it is, however, insoluble in carbon bisulphide and in petroleum ether. It is only slightly soluble in water; 100 c.c. of water dissolve 7·17 grms. of triacetin at 15° C. (*Geitel*[1]). $n^{15}_{D} = 1{\cdot}4328$ (*Partheil and v. Velsen*). 100 parts of cotton seed oil dissolve at the ordinary temperature about 10 parts of triacetin; 100 parts of butter fat dissolve, at 30° to 40° C., about 12 parts of triacetin (*Fincke*[2]).

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[1] According to Polenske's method, see Chap. V.

[2] Isolated from mutton tallow.

[3] Isolated from lard.

[4] When determining this point, the temperature of the bath in which the substance had been melted was kept for two hours at 58-59° C., was then allowed to cool to 40° C. and then heated afresh. Hence in the case of β-palmito-α-γ-distearin heating for about ten minutes at 52-55° C. does not suffice to convert the labile form of this glyceride completely into the stabile form. Tristearin and α-palmito-β-γ-distearin on the other hand show in other cases the same melting points (cp. Bömer, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (17), 361).

[5] *Proceed. k. Akad. v. Wetensch.*, Amsterdam, 1906, p. 109 ; *Zeits. f. phys. Chem.*, 1910 (70), 459 ; cp. also Béhal, *Ann. de Chim. et de Phys.*, 1900 (20), 411, and English patent 28,723, 1907 (Nitritfabrik Köpenick).

By the action of hydrobromic and hydrochloric acids on triacetin there are obtained α-α-dibromomonoacetin, α-α-dichloromonoacetin, α-β-dichloromonoacetin, and α-monobromoacetin respectively (*R. de la Acena*[3]). On treatment with sodium iodide α-mono-iodo-acetin is obtained.

Triacetin is stated[4] to occur in the oil of the seeds from *Evonymus europæa* (see table, Vol. II. Chap. XIV. "Lesser Known Semi-drying Oils"). Acetin (as also mono- and di-acetin) is said to be employed for gelatinising, and lowering the freezing point of, nitroglycerin (cp. Vol. III. Chap. XV.). Triacetin acts as a narcotic and has poisonous properties.

Tributyrin, Butyrin,[5] $C_3H_5(O\,.\,C_4H_7O)_3$. Tributyrin is the first glyceride that has been prepared synthetically (by *Pelouze and Gélis*[6]) by allowing gaseous hydrochloric acid or concentrated sulphuric acid to act on a mixture of butyric acid and glycerin. It is obtained on boiling one molecule of glycerol with three molecules of butyric acid for sixty hours (*Lebedeff*), or by heating dibutyrin with an excess of butyric acid for about twenty hours (*Berthelot, Guth*), or by allowing tribromohydrin and silver butyrate (*Partheil and v. Velsen*) to interact. Butyrin is a colourless liquid, does not solidify at – 60° C., and distils unchanged under a pressure of 24 mm. at 182°-184° C., and under the ordinary pressure at 287°-288° C. The following specific gravities and refractive indices are given by *Scheij*: $d^{20}_{4} = 1{\cdot}0324$; $d^{40}_{4} = 1{\cdot}0143$; $d^{60}_{4} = 0{\cdot}9963$; $n^{20}_{D} = 1{\cdot}48587$; $n^{40}_{D} = 1{\cdot}42785$; $n^{60}_{D} = 1{\cdot}42015$. The butyrin prepared by *Guth* indicated in the butyro-refractometer 12 "degrees" at 40° C. Butyrin is nearly insoluble in water, readily soluble in absolute alcohol and in 85 per cent alcohol, as also in the ordinary organic solvents. It is very doubtful whether butyrin occurs in butter fat as such; most likely the butyric acid radicle forms a constituent of a mixed glyceride. The taste of butyrin is intensely bitter.

Trivalerin, Valerin, $C_3H_5(O\,.\,C_5H_9O)_3$, obtained by heating synthetical divalerin with 8-10 parts of "valeric" acid to 220° C., is soluble in alcohol and ether. Valerin is said to be a characteristic constituent of dolphin and porpoise oils (see Vol. II. Chap. XIV.).

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[1] *Journ. f. prakt. Chem.* 55, 420.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xvi. 667.

[3] *Chem. Centralbl.*, 1905, i. 12.

[4] Schweizer, *Jahresb. f. Chem.*, 1857, 444.

[5] Triisobutyrin boils under the ordinary pressure at 282°-284° C., under a pressure of 24 mm. at 173°-176° C. In the butyro-refractometer it indicates 10·2 "degrees" at 40° C.

[6] *Nouv. Ann. de Chim. et de Phys.*, 1884 (10), 455.

Tricaproïn, *Caproïn*, $C_3H_5(O.C_6H_{11}O)_3$, prepared synthetically from glycerol and caproic acid, is a colourless, tasteless, and odourless liquid, solidifying at about −60° C., and liquefying at about −25° C. The following constants were determined by *Scheij* :—Specific gravity : $d^{20}_{4} = 0{\cdot}9817$; $d^{40}_{4} = 0{\cdot}9651$; $d^{60}_{4} = 0{\cdot}9494$. Refractive index : $n^{20}_{D} = 1{\cdot}44265$; $n^{40}_{D} = 1{\cdot}43502$; $n^{60}_{D} = 1{\cdot}42715$. Caproïn is miscible with 85 per cent alcohol, and the usual organic solvents at the ordinary temperature. It was stated to occur in cow butter, in cocoa nut and palm nut oils, and in elderberry oil ; but most likely the caproic acid radicle forms a constituent of a mixed glyceride.

Tricaprylin, *Caprylin*, $C_3H_5(O.C_8H_{15}O)_3$, obtained by heating glycerol with caprylic acid, is a colourless, tasteless, and odourless liquid, solidifying at −15° C. and melting at 8°-8·3° C. Its specific gravity, determined by *Scheij*, is : $d^{20}_{4} = 0{\cdot}9540$; $d^{40}_{4} = 0{\cdot}9382$; $d^{60}_{4} = 0{\cdot}9231$; its refractive index : $n^{20}_{D} = 1{\cdot}44817$; $n^{40}_{D} = 1{\cdot}44069$; $n^{60}_{D} = 1{\cdot}43316$. At the ordinary temperature caprylin is miscible with 85 per cent alcohol, as also with the usual organic solvents. Mixed glycerides containing the caprylic acid radicle form a characteristic constituent of cow butter, cocoa nut oil, palm nut oil, and elderberry oil.

Tricaprin, *Caprin*, $C_3H_5(O.C_{10}H_{19}O)_3$, has been prepared synthetically in the same manner as the two preceding glycerides. It forms crystals, melting at 31·1° C. Its specific gravity is $d^{40}_{4} = 0{\cdot}9205$; $d^{60}_{4} = 0{\cdot}9057$; its refractive index $n^{40}_{D} = 1{\cdot}44461$; $n^{60}_{D} = 1{\cdot}43697$. Caprin is soluble in the usual fat solvents at the ordinary temperature. It dissolves sparingly in absolute alcohol ; in the hot it is, however, easily soluble in this menstruum. Mixed glycerides containing the capric acid radicle form a characteristic constituent of cow butter, of cocoa nut and palm nut oils, of elderberry oil, and especially of elm seed oil, which is stated to yield 50 per cent of capric acid.

Trilaurin, *Laurin*, "*Laurostearin*," $C_3H_5(O.C_{12}H_{23}O)_3$, has been isolated from pichurim beans,[1] from laurel oil,[2] and from cocoa nut oil [3] by boiling the raw material with alcohol, or by fractional distillation of laurel oil *in vacuo* (*Krafft* [4]), or by crystallising tangkallak fat from ether (*van Eldik Thieme* [5]). According to *Sack*, it occurs also in the fat of the kernels of the Macasuba palm, "Kaumakka," (*Acrocomia sclerocarpa*, Mart.), and in the fruits of *Bactris Plumeriana*, Mart. (see Vol. II. Chap. XIV.). It is also stated to occur in the liver fat of a crustacean.[6] *Scheij* prepared it synthetically from glycerol and lauric acid ; and *Partheil and v. Velsen* from tribromohydrin and silver laurate. It crystallises in needles, melting at 45° C. ; 46·4° C. (*Scheij*). After being heated a few degrees above its melting point and allowed to solidify, it exhibits a lower melting point. Trilaurin prepared from the liquid α-α-dilaurin gave a liquid trilaurin which, curiously enough, gave in the cryoscopic method of determinating the molecular weight only half the theoretical value, whereas trilaurin prepared from the solid α-α-dilaurin, furnished normal trilaurin of the melting point 45° C. and of normal molecular weight (*Custodis*[1]). The specific gravity of trilaurin is $d^{60}_{4} = 0 \cdot 8944$ (*Scheij*); $d^{100}_{4} = 0 \cdot 8687$ (*Partheil and v. Velsen*); its refractive index $n^{60}_{D} = 1 \cdot 44039$. In the butyro-refractometer it indicates 31·5 " degrees " at 45° C.; 29 " degrees " at 50° C., and 24 " degrees " at 60° C. (*Partheil and v. Velsen*). It is sparingly soluble in cold absolute alcohol, but dissolves readily in ether. Trilaurin boils *in vacuo* at 260°-275° C. (*Krafft*[2]). Laurin is a characteristic constituent of laurel oil and especially of the fats belonging to the " cocoa nut oil group " and the " Dika Fat Group " (see Vol. II. Chap. XIV.).

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[1] Stahmer, *Liebig's Annal.*, 1845 (53), 390.

[2] Marsson, *Liebig's Annal.*, 1840 (41), 330.

[3] Görgey, *Liebig's Annal.*, 1848 (66), 290.

[4] *Berichte*, 1903, 4343.

[5] *Proceed. k. Akad. v. Wetensch.*, Amsterdam, 1908, 855 ; *Journ. f. prakt. Chem.*, 1912 (85), 285.

[6] *Chem. Zeit.*, 1895, 651.

Trimyristin, Myristin, $C_3H_5(O\,.\,C_{14}H_{27}O)_3$, occurs chiefly in the fats belonging to the " Myristica Group " (see Vol. II. Chap. XIV.). Virola fat consists to a very great extent, and ochoco fat almost exclusively, of myristin. Smaller quantities of this glyceride (perhaps in the form of a mixed glyceride) occur in human fat, lard, and butter fat. It has also been found in cochineal wax. Myristin has been obtained by fractional distillation of nutmeg butter *in vacuo* (*Krafft*[2]); it has also been prepared synthetically by the general methods described above. It crystallises from its ethereal solution in laminæ, melting at 56·5° C. (*Scheij*), 54°-55° C. (*Thoms and Mannich*[3]). When melted trimyristin is heated to 57°-58° C., it solidifies to a porcelain-like mass, melting at 45°-55° C.; on raising the temperature slightly for a very short time, it solidifies and regains the original melting point, viz. 56·5° C. On warming the porcelain-like mass in a bath having the temperature of 35°-45° C. it softens, becomes milky and solidifies, to melt again at 56·6° C. Trimyristin boils *in vacuo* from 290°-300° C. (*Krafft*[2]). Its specific gravity is $d^{60}_{4} = 0 \cdot 8848$ and its refractive index $n^{60}_{D} = 1 \cdot 44285$. Trimyristin is easily soluble in ether, benzene, chloroform, and hot absolute alcohol.

Tripalmitin, Palmitin, $C_3H_5(O\,.\,C_{16}H_{31}O)_3$, was discovered by *Fremy*, and was for a long time known as " margarin," especially in the French literature. It is obtained synthetically by heating (1) monopalmitin or dipalmitin with palmitic acid; (2) a mixture of glycerol and palmitic acid; (3) tribromohydrin with sodium (or silver) palmitate. It dissolves with very great difficulty in cold alcohol, more easily in hot alcohol; it is also sparingly soluble in cold ether. From hot ether it crystallises in needles, melting at 63°-64° C. (*Chittenden*); 65·1° C. (*Scheij*); 65·5° C. (*Guth*), 65° C. (*Bömer*[4]), and solidifying at 45°-47° C. If the crystals are heated to 70° C. and allowed to solidify, they melt a little above 45° C., then solidify again, and finally melt at 65·1° C.[5] Tripalmitin boils *in vacuo* from 310° to 320° C. with decomposition (*Krafft*). If the heating bath be kept above 360° C., palmitin distils *in vacuo* at 280° C. (*Caldwell and Hurtley* [1]). The specific gravity is $d^{80}_{4} = 0{\cdot}8657$; the refractive index $n^{80}_{D} = 1{\cdot}43807$. Tripalmitin occurs in many oils and fats, and is the preponderant constituent of palm oil, Japan wax, and myrtle wax.

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[1] *Inaug. Dissert.*, Zürich, 1909; Grün, *Berichte*, 1912, 3693.

[2] *Berichte*, 1903, 4343.

[3] *Ber. d. deutsch. pharm. Gesellsch.*, 1901, 264.

[4] *Journ. Chem. Soc.*, 1909, 856.

[5] Cp. R. Kremann and R. Schoulz., *Monatsh.*, 1912 (33), 1063.

Triheptadecylin, Heptadecylin, $C_3H_5(O.C_{17}H_{33}O)_3$, prepared synthetically by *Bömer and Limprich* [2] from heptadecylic acid, melts at 62·7° C. (transition point 51·0° C.). It crystallises from ether in microscopical needles, arranged in druses. 100 c.c. of ether dissolve at 0° C. 0·0288 grms. and at 15° C. 0·322 triheptadecylin.

Tristearin, Stearin, $C_3H_5(O.C_{18}H_{35}O)_3$, is obtained by heating (1) monostearin with 15-20 parts of stearic acid for three hours at 275° C. (*Berthelot*); (2) glycerol with an excess of stearic acid (*Scheij*); (3) distearin with stearic acid (*Guth*); (4) tribromohydrin with silver or sodium stearate (*Partheil and v. Velsen; Guth*). Stearin is less soluble in cold alcohol than is palmitin; from solutions of tristearin in boiling alcohol the dissolved substance separates nearly completely on cooling. It dissolves sparingly in *cold* ether and *cold* petroleum ether (more readily if the solvents are heated); in benzene and chloroform it dissolves readily in the cold. The stearin obtained by crystallisation from ether melts at 71·6° C., 72·2° C. (*Bömer* [3]), and solidifies at 70° C. to an indistinctly crystalline mass. The crystallised stearin exhibits only one melting point; if the crystals are heated above this melting point—by at least four degrees—they solidify at about 52° C. to a wax-like substance, melting at 55° C.; on further heating a few degrees above this latter point, the melting point 71·6° C. is again observed.[4] The specific gravity of a (not quite pure) specimen of stearin in the melted state was found to be 0·9235 at 65·5° C.; *Scheij* gives $d^{80}_{4} = 0{\cdot}8621$. The refractive index n^{80}_{D} is 1·43987 (*Scheij*). Stearin indicates in the butyro-refractometer 34 "degrees" at 55° C., and 23·5-24·5 "degrees" at 75° C. (*Partheil and v. Velsen*; *Guth*). It distils unchanged *in vacuo* (*Chevreul*). Stearin occurs chiefly in solid fats. *Bömer* [5] found in beef tallow only 1½ per cent and in mutton tallow only 3 per cent of pure stearin.

The (partial) conversion of stearin into ethyl stearate by boiling with a solution of sodium in absolute alcohol was first observed by *Duffy*; [6] the same change was noted by *Bouis* [7] on heating stearin with small quantities of alcoholic potash, insufficient to effect complete saponification. On substituting amyl alcohol for ethyl alcohol, amyl stearate is obtained (cp. p. 102). By the interaction of tristearin with chlorosulphonic acid there are obtained amongst other non-identified products distearin and stearic acid (*Corelli* [8]).

Triarachin, Arachin,[9] $C_3H_5(O.C_{20}H_{39}O)_3$, (prepared by *Berthelot* from diarachin and arachidic acid) is very slightly soluble in ether. Arachin occurs (most likely as a mixed glyceride) in arachis oil, and in smaller quantities in rape oil and butter fat.

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[1] *Journ. Chem. Soc.*, 1909, 856.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, xxiii. 653.

[3] *Ibid.*, 1909, xvii. 354.

[4] Cp. R. Kremann and R. Schoulz., *Monatsh.*, 1912 (33), 1063.

[5] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 90.

[6] *Journ. Chem. Soc.*, 1852, 303.

[7] *Compt. rend.*, 1862 (45), 35.

[8] *Inaug. Dissert.*, Zürich, 1909.

[9] It may be pointed out that Moser (*Landw. Versuchst.*, 1904, 321) gave the name "arachin" to an alkaloid found by him in the seeds of *Arachis hypogaea.*

Tricerotin, Cerotin, $C_3H_5(O.C_{26}H_{51}O)_3$, has been prepared by *Marie* from dicerotin. It crystallises in slender needles, melting at 76·5°-77° C. Cerotin is stated to occur in the fatty oil from *Aspidium Filix mas.*[1]

Trimelissin, Melissin, $C_3H_5(O.C_{31}H_{59}O)_3$, obtained from dimelissin (*Marie*[2]), resembles cerotin; it melts at 89° C. Hitherto it has not been found in nature.

(*b*) *Simple Triglycerides of Unsaturated Fatty Acids,* $C_nH_{2n-2}O_2$

Triolein, Olein, $C_3H_5(O.C_{18}H_{33}O)_3$, is obtained by heating glycerol with an excess of oleic acid at 240° C. for four hours (*Berthelot*); it may also be prepared by heating tribromohydrin with sodium oleate in a sealed tube to 180° C. *Pottevin*[3] prepared olein by the action of pancreatic ferment on mixtures of mono-olein and oleic acid at 36° C. Olein is an almost colourless, tasteless liquid, which solidifies at $-4°$ to $-5°$ C. On standing for several weeks, triolein solidifies at the ordinary temperature to an opaque mass (*Guth*). Olein distils *in vacuo* without decomposition (*Chevreul*). According to *Caldwell and Hurtley*[4] the distillation of olein commences *in vacuo* at 230° C. if the temperature of the bath surrounding the olein is kept at 350° C. The specific gravity of olein at 15° C. is 0·900. In the butyro-refractometer it indicates 56·5 " degrees " at 40° C. It dissolves easily in ether and is more readily soluble in absolute alcohol than either palmitin or stearin; it is insoluble in dilute alcohol.

Olein combines with concentrated sulphuric acid to form a saturated compound having the formula $(C_3H_5)_2(O.C_{18}H_{34}O.SO_4.C_{18}H_{34}O.O)_3$;[5] this substance is very unstable, and, on treatment with alcohol, is partly dissociated into H_2SO_4 and κ-hydroxystearic acid. Olein is converted into elaïdin under the same conditions under which oleic acid is converted by nitrous acid into elaïdic acid (p. 188). Olein absorbs bromine and iodine quantitatively to form hexabromo-olein and hexaiodo-olein (see Chap. VI.). In an atmosphere of ozone olein absorbs ozone, and forms the ozonide of olein (*Molinari and Fenaroli*; *Harries*; cp. Chap. III.).

Triolein-ozonide, $C_{57}H_{104}O_{15}$, is best prepared by passing a current of ozonised air through triolein dissolved in (petroleum) hexane, and driving off the solvent by warming the product of reaction on a water-bath *in vacuo.* The product represents a viscous, almost jelly-like, colourless oil, soluble in ether, acetic acid, benzene, and chloroform. It is decomposed by heating to 136° C. By treating with concentrated alcoholic caustic potash, in addition to azelaïc and nonylic acids, are obtained glycerol[6] (cp. " Oleic Acid," Chap. III.).

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[1] *Arch. d. Pharm.*, 1898, 655.

[2] *Journ. Chem. Soc.*, 1896, Abstr. i. 347.

[3] *Compt. rend.*, 1904 (138), 378.

[4] *Journ. Chem. Soc.*, 1909, 856.

[5] Cp. also Juillard, *Journ. Soc. Chem. Ind.*, 1894, 820, and below Chap. II.

[6] Molinari and Fenaroli, *Berichte*, 1908, 2790.

For the interaction of olein and mercuric acetate in acetic acid solution, cp. *A. Leys.*[1]

Olein occurs (probably as a mixed glyceride in many cases) in most oils and fats ; in preponderating quantity in the non-drying oils. Coula oil is stated to consist of almost pure olein.[2]

Trielaïdin, Elaïdin, $C_3H_5(O.C_{18}H_{33}O)_3$, crystallises in warts, melting point 32° C. (*Mayer*), 38° C. (*Duffy*). It dissolves readily in ether, but is nearly insoluble in alcohol.

Trierucin, Erucin, $C_3H_5(O.C_{22}H_{41}O)_3$, prepared by heating dierucin with erucic acid to 300° C., forms a crystalline mass, melting at 31° C. It is nearly insoluble in cold alcohol, but dissolves somewhat easily in boiling absolute alcohol ; it dissolves very readily in ether, benzene, and petroleum ether. Nitrous acid converts trierucin into tribrassidin. Erucin (in many cases probably a mixed glyceride containing the radicle of erucic acid), is a characteristic constituent of the oils belonging to the rape oil class. The solid constituent of the oil from *Tropæolum majus* is almost pure trierucin (*Gadamer*[3]).

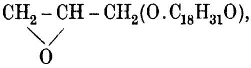
Tribrassidin, Brassidin, $C_3H_5(O.C_{22}H_{41}O)_3$, is a crystalline powder melting at 54°-54·5° C. If pure brassidin is heated above its melting point, even to 100° C., it still melts after cooling at 54°-54·5° C.

Tripetroselinin, Petroselinin, $C_3H_5(O.C_{18}H_{33}O)_3$, is obtained from parsley-seed oil as a crystalline mass, melting at 32° C., and solidifying at 16·50° C. ; $n_D^{40} = 14{,}619$ (*Vongerichten and Köhler*[4]). The iodine value of petroselinin was found at 84·3 (Theory for Olein, 86·2).

The following two (less unsaturated) triglycerides have been prepared synthetically.

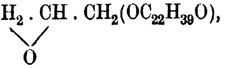
Tristearolin, Stearolin, $C_3H_5(O \,.\, C_{18}H_{31}O)_3$, obtained by heating trichlorohydrin with sodium stearolate to 190°-200° C. in a sealed tube, melts after recrystallisation at 29° C.

Hexabromotristearolin, $C_3H_5(O.C_{18}H_{31}Br_2O)_3$, is obtained by allowing bromine in a solution of carbon bisulphide to act on tristearolin (*Quensell*[5]).

Epistearolhydrin,  $CH_2-CH-CH_2(O.C_{18}H_{31}O)$, obtained by heating epichlorohydrin with sodium stearolate to 160° C., melts at 36° C.

Tribehenolin, Behenolin, $C_3H_5(O.C_{22}H_{39}O)_3$, obtained by heating trichlorohydrin with sodium behenolate in a sealed tube to 240° C., in an atmosphere of carbon dioxide, crystallises from alcohol in shining white leaflets, melting at 41° C. (*Quensell*[5]).

The *trichloro-iodo-behenolin,* $C_3H_5(O.C_{22}H_{39}ClIO)_2$, obtained from the chloroform layer in Hübl's test formed a thick oil (*Quensell*).

Epibehenolhydrin,  $CH_2 \,.\, CH \,.\, CH_2(OC_{22}H_{39}O)$, obtained by heating dichlorohydrin with sodium behenolate, and crystallised from petroleum ether or alcohol, melts at 43° C.

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[1] *Bull. Soc. Chim.*, 1907 (iv.), 543 ; cp. also *Journ. de Pharm. et Chim.*, 1907 (26), 289 ; Limprich, *Inaug. Dissert.*, Münster i/W., 1912.

[2] *Journ. Soc. Chem. Ind.*, 1895, 493.

[3] *Arch. d. Pharm.*, 1899 (237), 472.

[4] *Berichte*, 1909, 1638.

[5] *Ibid.*, 1909, 2445.

(*c*) *Simple Triglycerides of Hydroxylated Fatty Acids,* $C_nH_{2n-2}O_3$

Triricinolein, Ricinolein, $C_3H_5(O.C_{18}H_{33}O_2)_3$, occurs in castor oil. Ricinolein has been synthesised by heating glycerol with an excess of ricinoleic acid to 230° C. for six hours, unchanged glycerol and ricinoleic acid being removed by water and petroleum ether respectively.[1] If pressure and high temperature be employed, as is done in *Berthelot's* method, condensation products of mono- and diricinolein are formed, the simplest of which is isomeric with triricinolein, and has the formula $OH.C_{17}H_{32}.COO.C_{17}H_{32}.COO.C_3H_5(C_{17}H_{32}.COOH)_2$.

When triricinolein is heated in a solution of toluene, with or without zinc chloride, it is condensed to several esters (*e.g.* that represented by the formula $[(OH.C_{17}H_{32}.COO)_2C_3H_5.C_{17}H_{32}.CO]_2O$), which are differentiated from triricinolein by their sparing solubility in alcohol and petroleum ether.

H. Meyer[2] describes triricinolein (prepared by heating ricinoleic acid and glycerol in a current of carbon dioxide to 280°-300° C.) as a colourless oil (of the specific gravity 0·959-0·984 and having $[\alpha]_D = +5{\cdot}16°$), soluble in 96 per cent alcohol, and in methyl alcohol; miscible with absolute alcohol and glacial acetic acid; sparingly soluble in petroleum ether. Unlike castor oil, it does not form ricinelaïdin with nitrous acid. On keeping, it is stated to undergo polymerisation, the molecule becomng doubled or trebled, as is indicated by the increase of the specific gravity to 0·988-1·009, and the decrease of the iodine value from 71·84 to 44·7 (cp., however, "Castor Oil," Vol. II. Chap. XIV.).

The hydroxyl groups in the fatty acid radicles of ricinolein may be combined in their turn with acid radicles, so as to form esters. *Lidoff*[3] prepared the esters of formic, acetic, and stearic acids. The last-named compound having the composition $C_3H_5[O.C_{18}H_{32}O(O.C_{18}H_{35}O)]_3$ has also been synthesised by *Twitchell.*[4] The preparation of allophanic esters of ricinolein has been patented by *Vereinigte Chininfabriken Zimmer & Co.*[5]

Triricinelaïdin, Ricinelaïdin, $C_3H_5(O\,.\,C_{18}H_{33}O_2)_3$, obtained by treatng ricinolein (castor oil) with nitrous acid, crystallises in warts, which dissolve with difficulty in cold alcohol (*Playfair*[6]).

Mixed Triglycerides

Mixed triglycerides occur in the natural oils and fats to a very coniderable extent; in fact, it appears that they form the bulk of the vast majority of natural oils and fats. Their isolation from the natural products causes considerable difficulties, inasmuch as it would seem that the natural mixed glycerides undergo intramolecular changes whilst being treated with solvents.

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[1] Juillard, *Journ. Chem. Soc.*, 1895, Abstr. i. 500.

[2] *Journ. Soc. Chem. Ind.*, 1897, 633, 684.

[3] *Chem. Revue*, 1900, 127.

[4] *Journ. Amer. Chem. Soc.*, 1906, 196.

[5] German patent 211,197 (1907).

[6] *Liebig's Annal.*, 1847 (60), 322.

The synthetically prepared mixed triglycerides were obtained by methods similar to those employed in the preparation of simple triglycerides. It must, however, be pointed out that the products by no means represent the pure individuals aimed at. Thus *Kreis and Hafner*[1] state that when oleic acid is allowed to act on distearin or dipalmitin, considerable quantities of tristearin and tripalmitin are formed, whilst the yield of oleodistearin and oleodipalmitin is small. Furthermore *Bömer* has shown that the palmitodistearins (see below) described as pure substances still contained very considerable proportions of tristearin.

It would therefore follow that in the course of synthesising mixed glycerides by means of the methods described p. 11, intramolecular changes occur, which lead to the production of by-products and that all conclusions, based on identical melting points, as to the constitution must be considered as premature.[2]

Synthetically prepared mixed triglycerides also result in the course of the manufacture of hydrogenised fats (see below p. 59 and Vol. III. Chap. XV. "Hydrogenised (Hardened) Fats"). Theoretically all possible isomerides may be formed, so that triolein would yield tristearin on complete reduction of the oleic acid radicles, whilst less complete reduction would lead to the formation of monostearodi-olein and distearomono-olein.

A general method (proposed by *Grün and Schacht*[3]) for preparing *mixed glycerides* containing *two* different acid radicles consists in heating diglycerides with the anhydride of a fatty acid. Thus β-oleo-α-α-distearin was prepared by heating α-α-distearin and oleic anhydride under a pressure of 20·25 mm. to 170° C. for six hours, whilst a current of carbon dioxide was passed through the heated mass.

A general method for synthesising *mixed triglycerides* containing *three* different fatty acid radicles—which following the denomination adopted above (p. 18), are fixed by the positions α, β, and γ—consists in replacing in the molecule of α-monochlorohydrin, $C_3H_5Cl.(OH)(OH)$, at first the hydroxyl in the γ-position, then the chlorine in the α-position, and finally the hydroxyl group in the β-position successively by the acid radicles of three different fatty acids. Thus by allowing α-chlorohydrin to react with lauric chloride, there is obtained exclusively the diglyceride—*α-chloro-γ-laurin.*[4] (The γ-position of the lauric acid radicle is proved by the fact, that on replacing the chlorine atom by the hydroxyl group, α-monolaurin results.) By the action of potassium myristate the mixed diglyceride *α-myristo-γ-laurin* is formed, which, in its turn, by heating with stearic chloride, is converted into the mixed triglyceride *α-myristo-β-stearo-γ-laurin.* The latter may, of course, also be described as *α-lauro-β-stearo-γ-myristin.* By varying the order in which the fatty acid radicles are introduced, the three isomerides denominated by the general formulæ (3), (4), and (5) on p. 18, can be obtained. The three isomeric triglycerides indicated by theory for a triglyceride containing three different fatty acid radicles (p. 18), have been actually prepared in the case of the triglyceride of lauric, myristic, and stearic acids (see below).

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[1] *Berichte*, 1903, 2766.

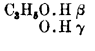
[2] Cp. Lewkowitsch Conférence, *Bull. Soc. Chim. de France*, 1909, iv.

[3] *Berichte*, 1907, 14.

[4] Grün and von Skopnik, *Berichte*, 1909, 3751.

It is noteworthy that a mixture of any two of the three isomerides, as also a mixture of all three isomerides, melt somewhat indistinctly, but in no case does the melting point lie below that of any of the components of the mixture, the melting point of any mixture lying between the melting points of the several components.

In order to place before the reader the configuration of the mixed glycerides described below in a synoptical manner, the positions of the several fatty acid radicles in the glycerol molecule will be denominated (cp. p. 11) by the letters α, β, γ, thus :—



$$C_3H_5\begin{array}{l}O.H\ \alpha\\ O.H\ \beta\\ O.H\ \gamma\end{array}$$

(*a*) *Mixed Triglycerides containing Acid Radicles of Saturated Fatty Acids only*

α-Aceto-β-γ-diformin, α-Acetodiformin, $C_3H_5(O.C_2H_3O)(O.COH)_2$, obtained by the action of the mixed anhydride of formic and acetic acids, $CH_3 . CO . O . CHO$,[1] on glycerol, is miscible with alcohol and ether in every proportion. $d^0 = 1{\cdot}249$. Under a pressure of 27 mm. it boils at 157° C.

β-Aceto-α-γ-dibutyrin, $C_3H_5(O . C_4H_7O)(O . C_2H_3O)(O . C_4H_7O)$, obtained by the interaction of acetodichlorohydrin and sodium butyrate, or by the action of α-α-dibutyrin on acetyl chloride, is a colourless oil of faint ethereal smell and aromatic bitter taste. It is miscible with alcohol and ether in every proportion. Under the ordinary pressure it boils at 289°-290° C., and under a pressure of 16 mm. at 173°-175° C. In the butyro-refractometer it indicates 5·3 " degrees " at 40° C.

β-Aceto-α-γ-dilaurin, $C_3H_5(O . C_{12}H_{23}O)(O . C_2H_3O)(O . C_{12}H_{23}O)$, obtained from solid *α-α-dilaurin* by heating it with acetic anhydride, crystallises from a mixture of ether and alcohol in white needles (*Custodis*).

β-Aceto-α-γ-dimyristin, $C_3H_5(O . C_{14}H_{27}O)(O . C_2H_3O)(O . C_{14}H_{27}O)$, obtained[2] by heating α-α-dimyristin with acetic anhydride for four hours, crystallises from ether partly in shining needles, melting 41·5° C., and partly in indistinct spheroidal crystals melting at 46·5° C.

α-Aceto-β-γ-dipalmitin, $C_3H_5(O.C_2H_3O)(O.C_{16}H_{31}O)(O.C_{16}H_{31}O)$, prepared[3] by heating dipalmito-α-chlorohydrin, $C_3H_5Cl.(O . C_{16}H_{31}O)_2$ [obtained from palmitic acid and α-chlorohydrin disulphonic ester, $C_3H_5Cl(O . SO_3H)_2$], with silver acetate in a sealed tube at 140° C. for three hours, melts at 67° C.

β-Aceto-α-γ-dipalmitin, $C_3H_5(O . C_{16}H_{31}O)(O . C_2H_3O)(O . C_{16}H_{31}O)$, obtained[3] by heating α-α-dipalmitin with acetic anhydride, melts in its crystalline state at 49° C. and solidifies at 29° C. The once melted crystals have the (constant) melting point of 33° C.

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[1] Béhal, *Compt. rend.*, 1899, 128, 1460.

[2] Grün and Schacht, *Berichte*, 1907, 1786.

[3] Grün, *Berichte*, 1905, 2286.

α-Aceto-β-γ-distearin, $C_3H_5(O.C_2H_3O)(O.C_{18}H_{35}O)(O.C_{18}H_{35}O)$, obtained[1] by heating β-γ-distearo-α-chlorohydrin with silver acetate and acetic anhydride in a sealed tube to 140° C., crystallises from alcohol in the form of druses, melting at 44° C., and after solidification at 43° C. After several weeks the melting point rose to 48° C., but after the melted substance had solidified, the melting point was again 43° C.

β-Aceto-α-γ-distearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_2H_3O)(O.C_{18}H_{35}O)$, obtained[2] by heating α-α-distearin for four hours with acetic anhydride, forms white crystals, readily soluble in ether and chloroform, sparingly soluble in alcohol melting at 56·5° C.

β-Lauro-α-γ-dimyristin, $C_3H_5(O.C_{14}H_{27}O)(O.C_{12}H_{23}O)(O.C_{14}H_{27}O)$, obtained[3] from α-α-dimyristin and lauryl chloride, forms microcrystalline, white granules melting at 46·5° C. A second modification of this glyceride, which melted at 36·5° C., is stated to have been isolated from the mother liquor of the crystals melting at 46·5° C.

α-Lauro-β-γ-dimyristin, $C_3H_5(O.C_{12}H_{23}O)(O.C_{14}H_{27}O)(O.C_{14}H_{27}O)$, is formed, together with β-myristo-α-γ-dilaurin (see below), by allowing myristyl chloride to act on α-α-dilaurin.[4] It is also obtained[5] by the action of dimyristo-α-chlorohydrin on potassium laurate. The product furnished by the former method is liquid, that obtained by the latter method is crystalline and melts at 45° C., and after solidification at 42·5° C. After several weeks' standing it melts at 43·5° C., and after solidification at 40° C.

α-Myristo-β-γ-dilaurin, $C_3H_5(O.C_{14}H_{27}O)(O.C_{12}H_{23}O)(O.C_{12}H_{23}O)$, prepared[6] from dilauro-α-chlorohydrin and potassium myristate, crystallises from alcohol in needles, melting at 41° C., and after solidification at 36·5° C.

β-Myristo-α-γ-dilaurin, $C_3H_5(O.C_{12}H_{23}O)(O.C_{14}H_{27}O)(O.C_{12}H_{23}O)$, is obtained,[7] together with α-lauro-β-γ-dimyristin (see above), by the action of myristyl chloride on α-α-dilaurin, in two isomeric modifications:—viz. a labile form crystallising in white plates, melting at 32° C., and a stable form, representing a microcrystalline powder, melting at 32-38·5° C., and after solidification at 36·5° C. The stable form is more sparingly soluble in all solvents than the labile form. The latter can be gradually converted into the stable form by inoculating an ethereal solution of the labile form with crystals of the stable form.

α-Stearo-β-γ-dilaurin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{12}H_{23}O)(O.C_{12}H_{23}O)$, obtained[8] from dilauro-α-chlorohydrin and potassium stearate, crystallises from alcohol in fine needles, melting at 46° C., and after solidification at 44° C.

β-Stearo-α-γ-dilaurin, $C_3H_5(O.C_{12}H_{23}O)(O.C_{18}H_{35}O)(O.C_{12}H_{23}O)$, obtained, together with α-lauro-β-γ-distearin, by the action of stearyl chloride on dilaurin, forms small white crystals, melting at 37·5° C.

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[1] Grün and Theimer, *Berichte*, 1907, 1795.

[2] Grün and Schacht, *ibid.*, 1907, 1781.

[3] *Ibid.*, 1907, 1787.

[4] *Ibid.*, 1907, 1790.

[5] Grün and Theimer, *ibid.*, 1907, 1798.

[6] *Ibid.*, 1907, 1799.

[7] Grün and Schacht, *ibid.*, 1907, 1790.

[8] Grün and Theimer, *ibid.*, 1907, 1799.

α-Lauro-β-γ-distearin, $C_3H_5(O . C_{12}H_{23}O)(O . C_{18}H_{35}O)(O . C_{18}H_{35}O)$, obtained,[1] together with β-stearo-α-γ-dilaurin, by the action of stearyl chloride on dilaurin, melts at 52·5° C.; after being kept for some time its melting point rose to 69·5° C. The product, prepared by heating α-chloro-distearin with potassium laurate to 175°-180° C. in a current of carbon dioxide for six hours, melted in its crystalline state at 49° C., and after solidification at 47° C.[2]

β-Lauro-α-γ-distearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{12}H_{23}O)(O.C_{18}H_{35}O)$, is obtained from α-α-distearin and lauric anhydride (prepared from lauric acid and acetic anhydride). On crystallising the product from alcohol to remove distearin and lauric acid, and recrystallising repeatedly from ether (30 to 35 times), two isomeric modifications are obtained—viz. a labile form, melting at 53·5° C., and a stable form, melting at 68·5° C. By inoculating the alcohol-ether solution of the labile form with crystals of the stable form, the former can be converted completely into the higher melting isomeride. In the cryoscopic determination of the molecular weight the stable form showed double the molecular weight; in the "boiling point" method uncertain results were found. The stable form could not be converted into the labile form.

α-Lauro-β-stearo-γ-myristin, $C_3H_5(O.C_{12}H_{23}O)(O.C_{18}H_{35}O)(O.C_{14}H_{27}O)$, prepared[2] by heating the diglyceride α-lauro-γ-myristin with stearyl chloride, crystallises in flocks melting at 37°-38° C.; after solidification the mass melts at 35° C.

α-Stearo-β-myristo-γ-laurin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{17}H_{27}O)(O.C_{12}H_{23}O)$, similarly obtained from the diglyceride: α-stearo-γ-laurin and myristyl chloride,[2] crystallises in granular masses melting at 48°-49° C.; after keeping for some time the crystals melt at 46° C. The solidified mass melts again at 44°-45° C.

α-Stearo-β-lauro-γ-myristin, $C_3H_5(OC_{18}H_{35}O)(OC_{12}H_{23}O)(O.C_{14}H_{27}O)$, prepared[2] from the diglyceride α-stearo-γ-myristin and lauryl chloride, forms indistinct crystals, melting at 42° C.; the solidified mass melts at 32° C

α-Myristo-β-γ-distearin, $C_3H_5(O.C_{14}H_{27}O)(O.C_{18}H_{35}O)(O.C_{18}H_{35}O)$, is prepared[3] by heating α-chloro-distearin with dry potassium myristate to 175°-180° C. in a current of carbon dioxide for six hours. It crystallises from alcohol (in which it is very sparingly soluble) in needles, melting at 52° and 62° C., and after solidification at 59° C.

β-Myristo-α-γ-distearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{14}H_{27}O)(O.C_{18}H_{35}O)$, is obtained[4] from α-α-distearin and myristic anhydride in two modifications:—a labile form (melting point 57° C., after solidification 55·5°) and a stable form (melting point 58·8° and 65° C., after solidification 58·5° C.). The two forms are separated by repeated recrystallisations—35 to 40 times—from ether, chloroform, benzene, and other solvents. By inoculating the labile form with crystals of the stable form, the melting point rose gradually. The molecular weight of the labile form was found in the cryoscopic method to be normal, whereas the stable

[1] Grün and Schacht, *Berichte,* 1907, 1791.

[2] Grün and Skopnik, *ibid.,* 1909, 3757.

[3] Grün and Theimer, *ibid.,* 1907, 1797.

[4] Grün and Schacht, *ibid.,* 1907, 1784.

form gave values leading to double the molecular weight. In the boiling point method the stable form furnished uncertain results.

α-Palmito-β-γ-distearin, $C_3H_5(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)(O.C_{18}H_{35}O)$, prepared synthetically from α-monopalmitin and stearic acid (*Guth*), or from β-α-distearin and palmitic acid (*Kreis and Hafner*[1]), melted in the crystallised state at 63° C. In the butyro-refractometer it indicated 22·5 " degrees " at 75° C.

Bömer[2] isolated this glyceride in a pure state by a very long and exhaustive series of crystallisations from lard, in which it occurs to the extent of about 3 per cent. Its melting point is 68·0° C. (corrected 68·5°) and its " transition point " 57·3° (corrected 51·5°).

β-Palmito-α-γ-distearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)$, prepared from α-α-distearin and palmitic acid by heating to 180° C. under diminished pressure (*Kreis and Hafner*[3]) crystallised from ether in tufts, consisting of microscopic needles. It was stated that in the superfused state it has two melting points, viz. 52·2° C. and 62° C., whereas in the crystalline state it melts at 63° C. It would therefore very closely simulate α-palmito-β-γ-distearin. *Bömer*[4] has, however, shown that the substance prepared by *Kreis and Hafner* contained over 12 per cent of tristearin. Later *Bömer*[5] showed that a " palmito-distearin," obtained by *Kreis and Hafner*[6] from beef tallow contained about 15 per cent of tristearin. *Bömer* himself prepared from mutton tallow by systematic crystallisation a palmitodistearin of the melting point 63·3° C.[2]

If the β-palmito-α-γ-distearin[7] is prepared synthetically from α-α-distearin and palmitic acid, there are formed simultaneously tristearin and α-stearo-β-γ-dipalmitin.

α-Stearo-β-γ-dipalmitin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)(O.C_{16}H_{31}O)$, prepared synthetically by *Guth* from α-monostearin and palmitic acid, crystallises in long rhombic plates, melting at 60° C. In the butyro-refractometer it indicates 27 " degrees " at 75° C.

β-Stearo-α-γ-dipalmitin, $C_3H_5(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)$, obtained synthetically from α-α-dipalmitin and stearic acid, crystallises in laminæ melting at 60° C. ; in the butyro-refractometer it indicates 24 " degrees " at 75° C.

A *stearodipalmitin (dipalmitostearin)*, $C_3H_5(O.C_{18}H_{35}O)(O.C_{16}H_{31}O)_2$, prepared by *Hansen*[8] from tallow, was described as crystallising in scales of silky lustre melting at 55° C. This substance differs in melting point from the two preceding isomerides, although it should be identical with one of them. It is therefore very likely that this " stearodipalmitin " still contained some tristearin. A stearodipalmitin, obtained by very frequently repeated crystallisations from mutton tallow, melts at 57·3° C. (*Bömer*[9]).

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[1] *Berichte*, 1903, 1123.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 393, 1913, xxv. 354. Cp. also Chap. XII.

[3] *Ibid.*, 1904, vii. 665.

[4] *Ibid.*, 1909, xvii. 359.

[5] *Ibid.*, 1907, xiv. 106.

[6] *Berichte*, 1903, 1123.

[7] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913, xxv. 353.

[8] *Arch. f. Hygiene*, 1902 (42), 1.

[9] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 391. Cp. also Chap. XII.

(*b*) *Mixed Triglycerides containing Acid Radicles of Saturated Fatty Acids and of Unsaturated Fatty Acids of the Series* $C_nH_{2n-2}O_2$

The existence of a *myristopalmitoolein*, $C_3H_5(O.C_{14}H_{27}O)(O.C_{16}H_{31}O)(O.C_{18}H_{33}O)$, stated by *Klimont*[1] to occur in cacao butter, and to melt in the crystalline state at 25°-27° C., must be regarded as doubtful (cp. "Cacao Butter," Vol. II. Chap. XIV.).

The identity of an *oleodipalmitin* (*dipalmitoolein*), $C_3H_5(O.C_{18}H_{33}O)(O.C_{16}H_{31}O)_2$, isolated by *Hansen* from tallow, by fractional crystallisation, and stated to melt at 48° C., is doubted by *Kreis and Hafner*.[2] On preparing β-oleo-α-γ-dipalmitin from α-α-dipalmitin, *Kreis and Hafner* obtained an oleodipalmitin which became translucent in a capillary tube at 20° C., and melted to a clear liquid at 38°-39° C. In the crystalline state it melted at 38°-39° C. The γ-oleo-α-β-dipalmitin obtained from α-β-dipalmitin became translucent at 18° C., and melted to a clear liquid at 37°-38° C. In the crystalline state it melted at 38° C. An oleodipalmitin melting at 29·2° C. was stated to have been obtained by the repeated crystallisation of vegetable tallow from acetone (*Klimont*[3]). An oleodipalmitin obtained in the same manner from Borneo tallow is stated to melt at 28°-29° C., and when freshly crystallised at 33°-34° C.

An *oleopalmitostearin* (*stearopalmitoolein*), $C_3H_5(O.C_{18}H_{33}O)(O.C_{16}H_{31}O)(O.C_{18}H_{35}O)$, obtained (from tallow) by *Hansen*[4] melted at 42° C. *Klimont*[1] claimed that he had isolated the same glyceride melting at 31°-33° C. from cacao butter, but withdrew this statement subsequently.

Oleodistearin, $C_3H_5(O.C_{18}H_{33}O)(O.C_{18}H_{35}O)_2$. This, the first known mixed glyceride, was obtained by *Heise* from mkányi fat and from kokum butter, by precipitating ethereal solutions of these fats with alcohol. It is also stated to occur in cacao butter (*Fritzweiler*[5]) and in Borneo tallow (*Klimont*[6]). It forms small white crystals readily soluble in boiling alcohol, sparingly soluble in cold alcohol. The crystals melt at 44°-44·5° C. and solidify at 40·8° C. If the melted glyceride is cooled rapidly, it melts at 27°-28° C.; on further heating, the substance solidifies again, finally to melt at 37°-38° C. The specific gravity at 70° C. is 0·8928, and at 90° C. 0·8547. According to *J. Sack*[7] the fat from *Mangifera indica* consists to a large extent of oleodistearin. The analytical data given for this fat do not bear out this contention.

The oleodistearin obtained synthetically by the action of oleic acid on α-α-distearin melts about 2°-4° C. lower than does the natural oleodistearin from mkányi fat and kokum butter (*Kreis and Hafner*).

The iodo-chloroderivative of oleodistearin was isolated by *Henriques and Künne*.[8]

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[1] *Monatsh. f. Chem.*, 1902, 231, 51.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1904, vii. 665.

[3] *Monatsh. f. Chem.*, 1903, 408; 1904, 931; 1905, 563.

[4] *Arch. f. Hygiene*, 1902, 42, 1.

[5] *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1902, 371.

[6] *Monatsh. f. Chem.*, 1904, 929; 1905, 563.

[7] *Pharm. Weekblad*, 1911, No. 13.

[8] *Berichte*, 1899, 390.

Grün and Schacht[1] prepared a *β-oleo-α-γ-distearin* by heating α-α-distearin with an equal amount of oleic anhydride for six hours to 170° C. at a pressure of 20 to 25 mm., whilst a current of carbon dioxide was passed through the mass. This oleodistearin melted, shortly after being prepared, at 42° C.; after being kept for one year it melted at 41° and at 55° C.; after solidification it melted at 42° C.

Elaidodistearin, $C_3H_5(O.C_{18}H_{33}O)(O.C_{18}H_{35}O)_2$, obtained by the action of nitrous acid on oleodistearin (*Henriques and Künne*[2]) melts at 61° C.

Dioleostearin, $C_3H_5(O.C_{18}H_{33}O)_2(O.C_{18}H_{35}O)$, has been stated (*Partheil and Ferié*[3]) to occur in human fat.

(c) *Mixed Triglycerides containing Acid Radicles of Saturated Fatty Acids and of Unsaturated Fatty Acids of the Series* $C_nH_{2n-4}O_2$

α-Linolo-β-γ-dipalmitin, $C_3H_5(O.C_{18}H_{31}O)(O.C_{16}H_{31}O)(O.C_{16}H_{31}O)$, from α-β-dipalmitin and linolic anhydride (with a very poor yield) melts at 11·5-13° C. (*H. Schoenfeld*[4]).

β-Linolo-α-γ-dipalmitin, $C_3H_5(O.C_{16}H_{31}O)(O.C_{18}H_{31}O)(O.C_{16}H_{31}O)$, from α-α-dipalmitin, and linolic anhydride melts at 28-29° C. (*H. Schoenfeld*).

α-Linolo-β-γ-distearin, $C_3H_5(O.C_{18}H_{31}O)(O.C_{18}H_{35}O)(O.C_{18}H_{35}O)$, from α-β-distearin, and linolic anhydride forms white crystals melting at 33·5-37° C. (*H. Schoenfeld*).

β-Linolo-α-γ-distearin, $C_3H_5(O.C_{18}H_{35}O)(O.C_{18}H_{31}O)(O.C_{18}H_{35}O)$, from α-α-distearin and linolic anhydride melts at 41-42° C.; after solidification it melted again at 36° C. (*H. Schoenfeld*).

The occurrence of a mixed glyceride of japanic and palmitic acids having the formula $C_3H_5(C_{20}H_{40}[CO.O]_2)(O.C_{16}H_{31}O)$ in Japan wax is considered probable by *Geitel and v. d. Want* (see Vol. II. Chap. XIV. "Japan Wax").

Phosphatides

A large group of naturally occurring mixed triglycerides, containing as a rule two fatty acid radicles and one radicle of phosphoric acid, the latter in conjunction with an organic basis, are found widely distributed, although only in very small quantities in all tissues of vegetable and animal organisms. Their chemical composition may be represented by the general formula $C_3H_5(OR)(OR)(O.PO).(OH)(OB)$, wherein B stands for a monoamino base.

For these triglycerides the term *phosphatides* proposed by *Thudichum* has been accepted generally. (In order to denote the basic character of these substances *Leathes*[5] suggests the term "phospholipines.")

Phosphatides represented by this formula are denominated monoamino-mono-phosphatides on account of the nitrogen and phosphorus atoms standing in the proportion 1 : 1.

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[1] *Berichte*, 1907, 1782.

[2] *Ibid.*, 1899, 387.

[3] *Arch. d. Pharm.*, 1903, 545.

[4] *Inaug. Dissert.*, Zürich, 1912.

[5] *The Fats*, Longmans, Green & Co., 1910; cp. also O. Rosenheim, *VII. Intern. Congr. of Appl. Chem.*, 1910, vol. iv, art. 2, p. 56.

Although these glycerides appear to exercise a most important physiological function (in fact appear to some authors to be the real "life sustainers"), very little is known as to their actual importance in the economy of the vegetable and animal organism. Nor has their chemical composition been established, and many conflicting statements on this point are found in the literature of the subject.

The best known phosphatide is the *Lecithin*[1] which occurs in egg-yolk.[2] On saponification (with alcoholic potash or with hydrochloric acid[3]) it furnishes choline,[4] glycero-phosphoric acid, and fatty acids. Hence the following formula is generally ascribed to it: $C_3H_5(OR)(OR).[O.PO(OH)(O.CH_2CH_2N(CH_3)_3OH]$. According to *Willstätter and Lüdecke* lecithin is a derivative of an α-β-diglyceride. In the case of a specimen of egg-yolk lecithin prepared by *Cousin*,[5] the fatty acids obtained on saponification[6] are stated to consist of 24 per cent of linolic, 28·5 per cent of palmitic, and 14·2 per cent of stearic acid. *Rollett*[7] gives the iodine value of egg-lecithin as 62 to 69. The unsaturated fatty acids are capable of being reduced by means of hydrogen in the presence of a suitable catalyst (see "Hydrolecithin," p. 60).

The above given formula contains an asymmetric carbon atom, and in agreement therewith, natural lecithin is optically active. A (commercial) preparation of egg-lecithin examined by *P. Mayer*[8] had $[\alpha]_D = +9·84$. Like tartaric acid, mandelic acid,[9] etc., it is converted, on heating, into the racemic form, which was resolved (by means of steapsin) into its optically active stereoisomerides, of which the laevorotatory lecithin was isolated (*P. Mayer*[8]). This shows that the phosphoric acid radicle which carries the choline group is in the γ-position. (The glycerophosphoric acid, obtained at the same time, was also found to be optically active; *Willstätter and Lüdecke*.[10]) It should, however, be noted that *N. A. Barbier*[11] is of the opinion that egg-yolk does not contain lecithin.

Lecithin of a very similar composition[12] has been isolated from many plant seeds, especially those derived from the *Leguminosæ*,[1] and the cereal grains.

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[1] For a compilation of the literature on lecithin, cp. F. Kade, *Inaug. Dissert.*, Zürich, 1911. Grün and Kade, *Berichte*, 1912, 3358; 3367.

[2] First prepared by A. Strecker (*Liebig's Annal.* 148, 80). Cp. also Zuelzer, *Hoppe-Seyler's Zeits. f. physiol. Chem.* 27, 462.

[3] Cp. F. Malengreau and G. Prigent, *Zeits. f. physiol. Chem.*, 1912 (77), 107.

[4] For the preparation of choline from lecithin, cp. J. D. Riedel, German patent 193,449.

[5] *Journ. Pharm. Chim.*, 1903, 102; cp. also Henriques and Hansen, *Skand. Arch. f. Physiol.*, 1903, xiv. 390.

[6] For the saponification of lecithin by "alcoholysis," cp. Fourneau and Plettre, *Bull. Soc. Chim. de France*, 1912, v. (11), 805.

[7] *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1909 (61), 214.

[8] *Biochem. Zeits.*, 1905, 39.

[9] Lewkowitsch, *Berichte*, 1883, 2721.

[10] *Berichte*, 1904, 3753.

[11] *VII. Intern. Congr. of Applied Chemistry*, 1910, vol. iv. art. 2, p. 64. *Chem. Zeit.*, 1912, 985.

[12] Studied especially by Schulze, Winterstein and Hilstand, *Zeits. f. physiol. Chem.*, 1906 (47), 496.

For the commercial preparation of lecithin from cereals the reader must be referred to the patents given in the footnote.[2] *C. A. Fischer*[3] extracts vegetable and animal substances with ethyl acetate, methyl acetate, or methyl butyrate to remove fatty oil and cholesterol. The residue containing the lecithin (in the case of egg-yolk from 35 to 40 per cent of lecithin) is dried *in vacuo* and extracted with alcohol at 70° C. Lecithin separates from the solution on cooling.

Lecithin differs from the above described triglycerides—*i.e.* from true fats and oils—by its solubility in alcohol. It possesses the property of readily emulsifying water. Ether and similar solvents extract very little lecithin from emulsions, but the lecithin is immediately taken up by the solvent after addition of salts. Glycerol, dextrose, sucrose, and carbamide neither cause precipitation from the emulsions nor aid in the solution of the lecithin by ether. On the addition of traces of salt solutions to the mixtures the lecithin is immediately dissolved by the ether.[4]

Lecithin is insoluble in acetone and can therefore be precipitated from its solutions by acetone. It is slightly soluble in oils and fats, and hence is extracted together with the oils and fats in the commercial processes of preparing the latter. An indication as to the amounts of lecithin found in commercial oils and fats may be gathered from the table given in Chap. IV. "Estimation of Phosphorus."[5]

Lecithin from egg-yolk as also from cereals, etc., is employed in the margarine industry (see Vol. III. Chap. XV.), and in the preparation of cod liver emulsions and food compounds. Solutions of lecithin in glycerol[6] and in mono-, di-, and tri-chlorohydrin[7] are also being brought into commerce.

Lecithin, or rather lecithin-like substances, isolated from liver, muscles (heart muscles), kidney, brain, and nerves, and blood seem to have, generally speaking, a similar composition to that given above for the egg-yolk lecithin. Thus *Leathes*[8] has shown that the ether extract from active organs of the body (liver, heart, kidney) yields 65 per cent of insoluble fatty acids. Assuming that in the molecule of a lecithin of the formula given above, R be 280, it would follow that lecithin should yield 67 per cent (about) of insoluble fatty acids. The composition of the fatty acids appears, however, to be different, the " organ fats " apparently being characterised by the ease with which they undergo chemical changes in the body. *Erlandsen*[1] showed that the lecithin-like substances (" phosphatides ") isolated from the heart muscle (of the ox) contain less saturated acids than oleic. It is also noteworthy (although of minor importance for the purposes served by this work) that the iodine values of the organ fats are higher than those of the connective tissue fat. *Wolcke* states the following figures : Iodine value of the fat from the liver (of a dog) 83·1, from the heart muscle 84·9, from the kidney 78·0, whereas the iodine value of the connecting tissue fat was 62·8. *Hartley*[2] found that the fatty acids contained in these organs absorbed from 113 to 134 per cent of iodine. The unsaturated fatty acids appear to undergo oxidation somewhat easily on exposure to air, thereby becoming to some extent insoluble in petroleum ether. On separating the saturated fatty acids from the unsaturated acids (by the lead salt ether method) *Hartley* obtained unsaturated fatty acids (from pig and ox livers) having iodine values from 174 to 203. The bromide test led to the conclusion that the unsaturated acids contain acids belonging to the unsaturated series $C_nH_{2n-6}O_2$ and even $C_nH_{2n-8}O_2$ (see Chap. III.).

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[1] Cp. König and Schluckebier, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 650. For the quantitative determination cp. C. Fendler, *Apoth. Zeits.*, 1905 (3); Riedel, *ibid.*, 1905, 72.

[2] Blattmann, French patent 357,451; cp. also E. Ziegler, German patent 179,591; French patent 364,896; H. C. Buer, German patents 200,253, 210,013, 236,605; English patent 12,405, 1908; United States patent 1,055,514; Poulenc Frères, French patent 406,634. J. D. Riedel, Akt. Ges., German patent 260,886.

[3] English patents 11,597, 1908; 18,540, 1909; French patent 390,683.

[4] J. H. Long and F. Gephart, *Journ. Amer. Chem. Soc.*, 1908, 895.

[5] For the determination of lecithin in medicinal preparations cp. C. Virchow, *Chem. Zeit.*, 1911, 913; 1912, 906.

[6] P. Bergell, German patent 231,233.

[7] Deutsche Chem. Werke, "Victoria" and P. Salzmann, German patent 241,564.

[8] *Journ. of Physiol.*, 1907 (36), 19. Cp. also Bang, *Chemie u. Biochemie d. Lipoide.*

In an exhaustive examination of the fatty acids of lecithin from pig liver fat *Hartley*[2] isolated the following acids : Palmitic, stearic, an oleic acid differing from the ordinary oleic acid, linolic acid (possibly a mixture of two isomeric linolic acids), and an acid of the composition $C_{20}H_{32}O_2$. Linolenic could not be identified and is most probably absent.

The ready oxidisability of the fatty acids in the " organ fats " would seem to establish a relationship with the fatty acids contained in liver oils, and thus point to a fact of considerable importance, namely that these easily oxidised substances are constituents of those organs of the body which are the centre of greatest metabolic activity.

Mixed glycerides containing radicles of organic acids, other than those of naturally occurring fatty acids, as also mixed glycerides containing fatty acids radicles side by side with the radicles of inorganic acids, which have hitherto not been met with in nature, will be described under " Glycerol " (Chap. III.).

2. Properties of Natural Oils and Fats

The natural oils and fats are distributed throughout the vegetable and animal kingdom from the lowest organisms up to the most highly organised forms of vegetable and animal life, and are found in almost all tissues and organs. In plants, oils and fats are deposited in considerable quantities in the seeds, and are associated therein with starch, nitrogenous substances, etc., to serve as nourishment to the embryo. Exceptionally, oil has been found in considerable quantities in the rhizomes of *Cyperus esculentus*, L. (See Vol. II. Chap. XIV. table "Lesser Known Non-drying Oils."[1]) In the animal organisms oils and fats are mainly enclosed in the cellular tissues of the intestines and in the tissues nearest the outer skin (cp. Vol. II. Chap. XIV. "Animal Fats").—The further consideration of the "phosphatides" falls outside the scope of this work.

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[1] *Zeit. f. physiol. Chem.*, 1907 (11), 71.

[2] On the nature of the fat contained in the liver, kidney, and heart, *Journ. of Physiol.*, 1907 (36), 18.

The natural oils and fats may, for practical purposes, be looked upon as consisting in the main of mixtures, in varying proportions, of the triglycerides described above. Natural oils and fats must, therefore, not be looked upon as chemical individuals, but rather as representatives of natural species which, like all natural species, are subject to certain variations, although these be confined within comparatively narrow limits. Thus the composition of vegetable oils and fats derived from one and the same species of plant will fluctuate somewhat with the variety of the plant, the climate, and the soil in which it is grown, much as the composition of animal oils and fats varies with the race and age of the animal, and especially with the food.

No natural oil or fat consists of one simple triglyceride, although some of the vegetable fats derived from *Myristicaceæ* contain very small quantities only of fatty acids other than myristic. Thus ochoco fat (see Vol. II. Chap. XIV.) might be considered, for practical purposes, as consisting of pure myristin only. Until recently the natural oils and fats were looked upon as mixtures of at least two or three triglycerides, the most important of which were considered to be trilaurin, trimyristin, tripalmitin, tristearin, triolein, trilinolin, trilinolenin, triclupanodonin, and triricinolein, with which are admixed in much smaller quantities glycerides containing butyric acid (in butter fat), caproic, caprylic, capric acids (in butter fat, cocoa nut oil, palm nut oil), and arachidic acid (in arachis oil). In consequence of the discovery of mixed glycerides and the great difficulty of isolating pure triglycerides from the most frequently occurring fats and oils, it has become extremely likely that most natural oils and fats are composed chiefly of mixed triglycerides. At present our knowledge is still too limited to justify any definite expression of opinion as to the exact composition of the glycerides in the natural oils and fats.

The natural vegetable and animal oils and fats are prepared by comparatively crude methods (see Vol. II. Chap. XIII.). Hence they generally contain impurities of one kind or another, such as resinous, colouring, mucilaginous matter, remnants of vegetable and animal tissues,[2] etc. These can be removed for the most part by steaming or washing with water, followed by bleaching and filtering (cp. Vol. II. Chap. XIII.). But even after this purification small quantities of non-glyceridic substances remain dissolved. Some of these must be considered as entirely foreign (adventitious) substances, *e.g.* traces of colouring matters, chromogenetic substances (producing the colour reactions which are characteristic of some oils and fats), ethereal oils, resinous matters, sulphur compounds (in rape oil), and cyanogenetic glucosides as in linseed, para rubber seed, service berries, etc.[1]

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[1] The occurrence of glycerides in the soil (cp. O. Schreiner and E. C. Shorey, *Journ. Amer. Chem. Soc.*, 1911 (33), 78) is readily explained as due to accidental circumstances. These glycerides undergo natural processes of oxidation and hence yield on saponification dihydroxystearic acid.

[2] The small proportions of nitrogen occurring in commercial oils and fats would appear to be due to remnants of such tissues. G. Bouchard (*Compt. rend.*, 1912 [154], 1620) inclines to the opinion that nitrogen is a constituent of all oils and fats.

Other substances are *constant concomitants* of the natural products, and must therefore be looked upon, in a wider sense at least, as constituents thereof. The most important of these are *phytosterol* and *cholesterol*, inasmuch as the presence in, or the absence from, an oil or fat of one or the other "sterol" enables us to recognise a specimen as of vegetable or animal origin.

Other "sterols," such as bombicesterol, stigmasterol, and brassicasterol, are characteristic of individual oils and fats. *Volatile oils* again are contained to a notable extent in the fats belonging to the *Myristica* group. The volatile oil contained in crude cocoa nut oil has been identified as consisting principally of methylheptylketone and methylnonylketone (which occur also in the essential oil of rue). Less important, from the practical point of view of this work, amongst the constant constituents is lecithin, which occurs in fats and oils in extremely small quantities.

Midway between the last two groups—adventitious substances and constant concomitants—stand *hydrocarbons*,[2] and *aliphatic alcohols* (such as melissylalcohol and cerylalcohol). Probably these substances, forming as they do common constituents of vegetable and animal tissues occur more frequently in natural fats and oils than has been ascertained hitherto, as, on account of their small quantities, they have not been isolated and examined separately, being generally comprised, together with phytosterol and cholesterol, under the substances determined as "unsaponifiable matter." Hydrocarbons, which may possibly furnish a means of identifying individual oils and fats, have been isolated from parsley seed oil, laurel oil, cacao butter, kôsam seed oil and from cantharide oil, Melolontha oil (see Vol. II. under these headings). Indeed considerable amounts of hydrocarbons appear to be characteristic of all insect fats (see chrysalis oil, cantharide oil, Melolontha oil), as also of waxes from insects.

Also ketones, secondary alcohols (possibly formed from aldehydes), have been found in oils (cocoa nut oil), their presence doubtless being due to their slight solubility in the oil.

Oils and fats of vegetable origin, even in their fresh state, mostly contain appreciable quantities of free fatty acids. (*Rechenberg*[3] showed that the amount of free fatty acids is larger in unripe seeds than in ripe ones. In seeds which have been gathered in the unripe state chemical changes take place, resulting in a decrease of free fatty acids with the formation of more neutral fat.) This appears to be due to the fact that the seeds contain enzymes which hydrolyse glycerides

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[1] Cp. T. A. Henry, *Science Progress*, 1906, July.—C. Ravenna and M. Zamorani, *Atti Accad. d. Linc.*, 1910, 10 (ii.), 356.

[2] Cp. J. Klobb, J. Garnier, and R. Ehrwein, "Hydrocarbons of Vegetable Origin," *Journ. Chem. Soc.*, 1910, *Abstr.* ii. 1100.

[3] *Berichte*, 1881, 2217.

(cp. p. 49), carbonic acid, which is always present,[1] supplying the acid necessary for initiating hydrolysis (cp. p. 50). When sufficient water is present, the hydrolysis will progress somewhat rapidly. The exceptional occurrence of diërucin in rape oil is rightly ascribed by *Reimer*[2] to the fact that the rape seed from which that specimen of rape oil was obtained had become moist during transport.

Animal fats, when freshly rendered, contain but very small quantities of free fatty acids. For practical purposes they may therefore be considered as consisting entirely of neutral glycerides. If, however, the fats are exposed to the atmosphere, the formation of notable quantities of free fatty acids takes place readily (see below).

In their liquid state fats penetrate easily into the pores of dry substances; if dropped on paper they leave a translucent spot—*grease spot*—which cannot be removed by washing with water and subsequent drying (difference from glycerol spots).

A curious effect, caused by the presence of the minutest quantities of oils and fats, has been described by *Lightfoot.* Camphor, crushed between layers of paper without having been touched with the fingers, rotates when thrown on to water, but a trace of oil or fat on the surface of the water causes the rotation to cease immediately; it is sufficient to touch the water with a needle which has been passed previously through the hair.

Oils and fats in their pure state are odourless, colourless, and tasteless; and what is usually regarded as characteristic in these respects of the different oils and fats, is really due to the presence of extremely small quantities of foreign substances.

The specific gravity of oils and fats varies between the limits 0·910 and 0·970 at 60° F. (cp. table, Chap. V.).

The freezing points of those oils which are fluid at the ordinary temperature range from a few degrees above zero down to $-28°$ C. (linseed oil). The melting and solidifying points of the natural oils and fats are given fully in Vol. II. Chap. XIV. under the heading of each individual.

Oils and fats pass through all gradations of consistence, from oils which are fluid even below the freezing point of water, up to the hardest fats which melt at about 50° C. Hence no sharp distinction can be made between oils and fats (cp. p. 3). Nevertheless it is convenient to apply the term "oil" to those glycerides which are fluid below about 20° C., and the term "fat" to those which are solid above that temperature. Hard fats which have been melted by warming solidify somewhat slowly.

If the cooling takes place gradually, solid glycerides separate in a crystalline or semi-crystalline state, so that the liquid portion can be separated mechanically from the solid portion by filtering (filter-pressing). This operation is frequently employed on a large scale, *e.g.* in "demargarinating" edible oils (cotton seed oil) or "racking" oils

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[1] Cp. Urbain, *Compt. rend.* 139 (1904), 606; cp. also below.

[2] *Berichte*, 1907, 256.

(cod liver oil) (see Vol. II. Chap. XIII., Vol. III. Chap. XV.). The solid glycerides so obtained were formerly looked upon as consisting chiefly of stearin or palmitin (" margarine ") or mixtures thereof. Hence, in commerce all solid fats prepared in the manner described are termed " stearine " (" margarine " [1]). In consequence of the discovery of mixed glycerides, this view must be abandoned; further research will most likely show that the " stearines " differ chiefly in their contents of mixed glycerides.

The refractive power of oils and fats, their action on the plane of polarised light, their microscopic appearance, and other physical properties, including the viscosity of the oils and fats, will be dealt with in Chap. V.

Natural oils and fats in their fresh state may be considered as being completely insoluble in pure water, although traces are dissolved when they, especially the oils (liquid fats), are shaken with large quantities of water. On allowing the emulsions thus obtained to become clear by standing, subsequently separating the fat, filtering the aqueous layer, and shaking the latter with ether, a minute quantity of fat will be found to have passed into that solvent, and can be recovered by evaporating the ether. On the other hand, oils and fats dissolve a little water; this can be entirely expelled on warming above 100° C. Certain substances have the property of increasing considerably the emulsifying power of water if brought into intimate contact with oils and fats (see " Emulsified Oils," Vol. III. Chap. XV.).

With the exception of castor oil, oils and fats dissolve but very sparingly in cold *alcohol.* Boiling alcohol, however, dissolves somewhat larger quantities, especially of those oils and fats which contain glycerides of the lower fatty acids; on cooling, nearly all the dissolved fat separates out. (The separation of natural oils and fats into more easily soluble and sparingly soluble glycerides by means of alcohol is used as an analytical means in the examination of edible fats, cp. Chap. V.). The solubility is considerably increased by the presence of free fatty acids; if the amount of the latter be large, exceeding about 30 per cent, even cold alcohol will readily effect dissolution.

Oils and fats dissolve very readily in *ether, petroleum ether, carbon bisulphide, chloroform, carbon tetrachloride, trichloroethylene* (and its congeners [2]), *benzene,* and *paraffin oils.* Castor oil, however, forms an exception as regards petroleum ether and paraffin oils (cp. Vol. II. Chap. XIV. " Castor Oil "). Triacetin is insoluble in carbon bisulphide and in petroleum ether. Further information as regards solubility will be found in Chapter V.

The solutions of neutral oils and fats are without action on indicators (provided, of course, the solvents used have been completely freed from traces of acids).

Dry oils and fats do not suffer any loss when heated to a temperature of 120°-150° C. Oils and fats containing glycerides of lower fatty acids suffer loss at about 200° C.

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[1] Stearin, palmitin, acetin, etc. (spelt without an "e"), denote in this work the pure triglycerides, whilst under "stearine," "acetine," commercial products are understood, the composition of which differs considerably from the corresponding triglycerides.

[2] Cp. Vol. II. Chap. XIII.

Provided prolonged contact with air is avoided, most oils and fats can be heated to a temperature of about 250° C. without chemical change. (Some oils and fats become paler in consequence of the destruction of dissolved colouring matter, *e.g.* linseed oil.) On being heated above 250° C. up to 300° C. in the absence of air, some oils, especially the drying oils, undergo a change which is very likely due to polymerisation. Thus, tung oil (cp. Vol. II. Chap. XIV.) is converted into a gelatinous solid mass. The industry of preparing lithographic varnish is based on this reaction (Vol. III. Chap. XV.). In the case of castor oil, the chemical change even leads to the formation of solid products. The condensation can be assisted in some cases by the addition of " condensing agents," such as concentrated sulphuric acid, aluminium chloride, and zinc chloride (cp. Vol. III. " Polymerised Oils ").

When the heating is continued beyond 250° C., decomposition sets in, with the formation of volatile products, the most prominent of which is acroleïn. For this reason attempts made by several observers to distinguish or value fatty oils by their " flashing points," as is done in the case of mineral lubricating oils (see Vol. III. Chap. XV.), must be looked upon as having, as a rule, very little importance. In exceptional cases only, depending on the application of the oils and fats to certain technical processes, the flash point, as also the ignition point, must be taken into account.[1] The intense odour of acroleïn, which all fats emit on being heated above 300° C., is one of the most characteristic reactions, enabling one to distinguish rapidly fatty oils and fats from mineral and ethereal oils. Amongst the volatile products obtained on heating oils and fats to high temperatures have been found, in addition to volatile acids and sebacic acid,[2] hydrocarbons of the ethane, ethylene, and aromatic series (and perhaps also naphthenes), the quantity of which is considerably increased when the destructive distillation takes place under pressure. This fact lends strong support to the theory that petroleum hydrocarbons owe their origin to the destruction of oils and fats.[3] The vegetable fats generally offer greater resistance to this conversion into hydrocarbons under pressure than do animal oils and fats. If an optically active fat is distilled destructively the hydrocarbons formed exhibit optical activity (*Lewkowitsch*[4]). Before gas-making from coal was generally adopted, illuminating gas was frequently prepared from fatty oils[5] by distilling them destructively. If such distillation be carried out in the presence of solid substances, especially of such as may act as catalytic substances ("kieselguhr" or hydrosilicate), destructive decomposition of the oils and fats occurs at a lower temperature than in the absence of those solid substances. Thus *N. Hviid*[1] has shown that from 10 grms. of lard treated with 50 grms. of a hydrosilicate known as "Pfirschinger Erde" ("Franconit"), after heating to 250° C. for 45 minutes, 196 ccm. gas were evolved, whereas lard without "Franconit" had to be heated to 365° C., and only then after the lapse of 100 minutes evolution of gas commenced. Whereas lard alone could be heated (under the conditions of the experiment) to 375°-380° C. without any hydrocarbons passing over, the same treatment in the presence of "Franconit" yielded at 350° C. a distillate consisting chiefly of hydrocarbons. It would appear that the decomposition of the glycerides with formation of free fatty acids in the presence of the "earth" provided a sufficient amount of free fatty acids to act on calcium carbonate, most likely present in the earth, thus leading to the formation of lime soap, which is decomposed to hydrocarbons at a lower temperature than that at which the glycerides are broken down (cp. below, p. 141).

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[1] The flash points of fatty oils, provided all volatile impurities have been removed, lie in the neighbourhood of 500° F.

[2] Cp. Redtenbacher, *Liebig's Annal.*, 1840 (35), 190.

[3] Cp. Lewkowitsch, *Jahrbuch der Chemie*, 1907, xvii. 415.

[4] *Berichte*, 1907, 4161.

[5] The manufacture of gas from fatty oils was introduced by John Taylor in 1815. In this connection it may be interesting to state that Faraday discovered benzene in condensed gas made from whale oil. Even at present " oil gas " is made from cocoa nut oil in the Philippines; cp. also "Gasification of Castor Oil and of Cod Liver Oil," P. Dvorkovitch, *Journ. Soc. Chem. Ind.*, 1893, 409.

This view is confirmed by experiments *Hviid* made with oleic acid (cp. below, p. 180).

On exposure to the atmosphere oils and fats gradually undergo certain changes. As these changes are of great importance, both from the scientific and commercial point of view, it will be necessary to consider them at some length, devoting special attention to the influence which light, air, and moisture exert, separately and conjointly.

The action of light alone, whilst air and moisture are excluded, has hitherto not been studied thoroughly. It is well known that oils and fats acquire a paler colour under the influence of insolation, some oils even becoming colourless. The application of insolation to industrial purposes is well exemplified by the bleaching of linseed oil, cod liver oil, and olive oil under glass or in glass bottles (cp. Vol. II. Chap. XIII.). Since pure glycerides are themselves colourless, the light can only affect the foreign substances dissolved in them. This is further proved by the fact that insolated cotton seed oil does not reduce silver nitrate (in *Becchi's* test, Vol. II. Chap. XIV.) so readily as does cotton seed oil kept in the dark, and that exposure to light destroys those minute traces of chromogenetic substances which give rise to colour reactions that were for a long time, erroneously, considered as characteristic. Possibly this specific action of light is due to the ultra-violet rays it contains (see below). Other statements as to the effect of light, such as the development of greater heat in *Maumené's* test by oils exposed to sunlight, or the formation of small amounts of free fatty acids (*Ballantyne*[2]), still require verification, as the air was not excluded rigidly enough in those experiments upon which the conclusions were based; for even in corked bottles, kept in direct sunlight, diffusion of air through the cork takes place in course of time. Nor was the influence of temperature ascertained in these experiments. Therefore, the observed changes are most likely due to the joint influence of light and air, and probably also to that of moisture contained in the latter.

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[1] *Petroleum*, 1911 (6), 429.

[2] *Journ. Soc. Chem. Ind.*, 1891, 29.

The effect of light alone on oils has been studied by *Ritsert.*[1] His experiments proved that, provided air be rigidly excluded, as is the case in sealed glass tubes, even prolonged insolation is incapable of producing a change which would lead ultimately to rancidity. *Mjoën*[2] instituted similar experiments, but no definite conclusions can be drawn from them beyond the inference that the chemical change which takes place under the action of light in presence of air differs from that occurring in absence of light. There is no satisfactory evidence to support the contention that polymerisation of glycerides (*e.g.* in linseed oil) is produced by light alone ; it is desirable that our scanty knowledge on this subject be supplemented by systematic study.[3]

Röntgen rays are stated to be practically without action on oils and fats. Ultra-violet rays, however (" Uviol light "), seem to exert a strong bleaching effect, which is not confined to the chromogenetic substances, but appears to lead to hydrolysis of the glycerides and also, in given cases, to their polymerisation. The hydrogen peroxide formed under the influence of the " uviol light " exerts an oxidising action simultaneously (cp. Vol. III. Chap. XV. ; cp. also " Uviol Oils," Vol. II.).

The statement by some writers that " uviol light " converts oxygen into ozone, which latter acts on oils and fats, has been controverted by other observers.

When studying the effect of **air**[4] we must clearly discriminate between the influence of the ordinary atmosphere—which necessarily includes the action of oxygen, moisture, and light (diffused daylight, direct sunlight)—and the influence of dry air, to the exclusion of moisture and light. The effect of the atmosphere on oils and fats varies in a very marked degree with the chemical composition of the glycerides. As a general rule, it may be stated that the greater the proportion of unsaturated fatty acids in oils and fats (as measured by their iodine absorption, cp. Chapter VI.), the greater is their power to absorb oxygen. The chemical change is most marked in the case of drying oils ; it becomes gradually less pronounced with the decrease of the power of absorbing iodine, as we pass through the classes of semi-drying oils and non-drying oils down to the solid fats. Marine

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[1] *Untersuchungen über d. Ranzigwerden der Fette*, Inaug. Dissert., Berlin, 1890.

[2] *Forschungsber. über Lebensmittel*, etc., 1877, 195.

[3] Cp. Winkel, *Liège Congress*, 1905, sect. v. 387 ; Ditz, *Chem. Zeit.*, 1905, 709 ; Droste, *Apothek. Zeit.*, 1907 (22), 598.

[4] With regard to the solubility of air in fats, H. M. Vernon (*Proc. Roy. Soc.*, 1907, 79, B. 366) finds that 100 c.c. of olive oil, cod liver oil, and of lard, when shaken up with air, dissolve the following amounts of oxygen, nitrogen, and carbon dioxide :—

	Olive Oil.		Cod Liver Oil.		Lard.
	At 15° C.	At 87° C.	At 15° C.	At 37° C.	At 45° C.
	c.c.	c.c.	c.c.	c.c.	c.c.
Oxygen	2·28	2·33	2·29	2·22	2·33
Nitrogen . . .	5·26	5·19	5·06	5·08	5·11
Carbon dioxide . . .	0·20	0·16	0·21	0·21	0·13

(As to the connection of the solubility of air in fats and the "caisson-disease," cp. Vernon, *Lancet*, 1907.)

animal oils occupy a position similar to that of drying oils. The oxygen absorption power of the various oils and fats will be considered at length in Chapter VII.; therefore, a brief statement may suffice here. Drying oils thicken at first and form an elastic skin on the surface. If exposed in sufficiently thin layers, as for instance, if spread on wood or glass, they are finally converted into a transparent, yellowish, flexible substance, insoluble in water, alcohol, and also, to a very great extent, in ether. Whilst this energetic oxidation takes place, heat is developed to such a degree that if the drying take place in presence of organic substances in a fine state of division, offering a large surface to the atmosphere (cotton waste,[1] woollen rags), spontaneous combustion will ensue. The non-drying oils remain more or less unchanged. The semi-drying oils occupy an intermediate position. The gradations between the various classes are, however, by no means so distinct as to warrant the drawing of hard-and-fast dividing lines between the three classes.

The action of air is intensified by spreading oils and fats over finely divided metals[2] (lead powder, copper powder; see *Livache's* test, Chapter VII.), the metals acting as accelerators or catalysts (see Chap. VII. " Oxygen Absorption ").

If air under very high pressure is allowed to act on oils and fats the evolution of heat may rise to such an extent that the oils and fats are burnt up completely to carbon dioxide and water (Application of oils and fats in the Diesel Engine).

Dry air, to the exclusion of moisture and light, has no action on oils and fats. Therefore they will remain unchanged for practically an indefinite length of time if kept protected from moisture and light. It is very difficult to exclude the last traces of moisture when storing oils and fats; hence such traces of moisture may exercise a slight action in the manner described in the following paragraph, that is to say, small amounts of fatty acids will be formed, but no rancidity will set in. This is a matter of common experience, and has been demonstrated by *Lewkowitsch*[3] in the special cases of a linseed oil kept for thirteen years in bulk, and of a sample of cacao butter kept in a sealed bottle for ten years.

The effect of **moisture**, which is always present in the atmosphere, is a far-reaching one. In order fully to understand its effect, it is necessary to consider first the action of water on oils and fats.

At temperatures up to about 150° C. water does not attack glycerides, but if the temperature be raised to 200° C. or more, the triglycerides are finally decomposed (hydrolysed) into their proximate components, glycerol and fatty acids, whilst the elements of water are assimilated. This action appears to have been observed first by *Appert* in 1823. It is expressed by the following equation (cp. Chap. II.):—

$$C_3H_5(OR)_3+3H.OH=C_3H_5(OH)_3+3R.OH.$$

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[1] Cotton is much more liable to spontaneous combustion than are wool and silk.

[2] Cp. W. van Rijn, *Pharm. Weekblaad*, 1908, 346. (Action of sesamé and castor oils on zinc, and of olive oil on finely divided metals.)

[3] *Journ. Soc. Chem. Ind.*, 1899, 557.

The hydrolysis thus produced at high temperatures is greatly accelerated if the action of the water is assisted by suitable chemical agents (catalysts). If such agents are present, it is possible to reduce the temperature. Thus, by the assistance of concentrated sulphuric acid, the chemical change may be effected at a temperature of about 120° C. (True, some intermediate products are formed, but the full mechanism of the reaction need not concern us here, inasmuch as, on boiling with water, these intermediate products are ultimately decomposed into glycerol and fatty acids.) The temperature required for the chemical change may be further reduced to about 100° C. by employing strong hydrochloric acid.[1] A still further reduction of temperature can be effected by the introduction of strong bases in alcoholic solution (see Chap. II.).

Finally, the change may be brought about by water even at the ordinary temperature, if naturally occurring ferments, such as lipase[2] or steapsin,[3] are intimately intermixed with the oils and fats. Fat-hydrolysing enzymes seem to occur in most, if not in all, oleaginous seeds (see p. 42), and no doubt play an important part in the utilisation of the fatty reserve products stored in the seeds. During the germination[4] of the seeds, hydrolysis takes place, and free fatty acids are liberated; hence, it appears very likely that the presence of small quantities of free fatty acids, which are always found in, even the freshest, vegetable oils and fats (see p. 43), is due to the action of these enzymes on the glycerides stored in the seeds. The absence of suitable conditions in ungerminated seeds would appear to limit very sensibly the progress of hydrolysis. Such conditions are the presence of sufficient water and of small amounts of a mineral acid (carbonic acid, cp. p. 43), or of a strong fatty acid (such as acetic acid). If water acidulated with small quantities of such acids be churned up with oils and fats, and suitable enzymes be introduced, hydrolysis of the glycerides takes place gradually at first, but can be carried to a considerable extent within a comparatively short time (see Chap. II.). Thus, the ferment contained in castor seed[5] is capable of effecting practically complete hydrolysis in the course of a few days. Similarly acting ferments, such as "catalase,"[6] may reasonably be assumed to be contained in commercial animal fats to a less or greater extent, according to the care exercised in the separation of the animal tissue from the rendered fat. Indeed *Pagenstecher*[7] has shown since, that lipolytic ferments occur not only in the liver and intestines but also in the tissues of the body.

Accepting, then, as a fact the occurrence of small quantities of fat-hydrolysing enzymes in those commercial oils and fats which have not been heated to such temperatures that inhibition of the enzymic action must set in, we shall be able to understand those changes which oils and fats undergo on exposure to the atmosphere. As is well known, they thereby acquire a disagreeable smell and an acrid taste; and the presence of free, non-volatile fatty acids, as also of small quantities of volatile acids, can be observed. We comprise these changes under the term "rancidity," and we say: the oils and fats have become "rancid." In order to arrive at a satisfactory explanation of these changes, I propose to trace the effects of each of these agents in detail, step by step, and to examine how far such an explanation agrees with actual observations.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1903, 6.

[2] Cp. Green, *The Soluble Ferments and Fermentation*, Cambridge, 1899.

[3] Lewkowitsch and Macleod, *Proc. Roy. Soc.*, 1903 (72), 31; cp. Chap. II.; cp. also Lewkowitsch, "Les Corps gras. Conférence," *Bull. Soc. Chim. de France*, 1909, xv.

[4] Cp. D. Bruschi, "Ricerche fisiologiche sulla germinazione dei semi di Ricino," *Annali di Botanica*, 1908, 199.

[5] Connstein, Hoyermann, and Wartenberg, *Berichte*, 1902, 3988; Hoyer, *ibid.*, 1904, 1436.

[6] Cp. Liebermann, *Berichte*, 1904, 1519.

[7] *Biochem. Zeitsch.*, 1909, 305.

In the presence of sufficient moisture and acid, enzymes are capable of accelerating hydrolysis so that a certain proportion of the glycerides may give rise to the production of diglycerides, monoglycerides, and free fatty acids within a comparatively short time (a few days or a few weeks according to the special conditions). Hence the *first postulate is that free fatty acids should make their appearance.*

It is well known that oils and fats, if kept fully protected from light, air, and moisture, retain indefinitely[1] their state of neutrality, whereas if they are not carefully preserved, moist air easily gains access (as in imperfectly corked bottles, barrels, etc.), and free fatty acids, of the same composition as those which are combined with glycerol in the neutral fat, are produced. The quantity of enzymes in filtered commercial oils and fats being very small, the amount of hydrolysis effected thereby is restricted; hence the proportion of free fatty acids in commercial oils and fats does not, as a rule, exceed a few per cent. If, however, oils and fats be allowed to remain in contact with the organic matter from which they have been obtained, such as the marc of fruits (as in the case of olive oil, palm oil, cocoa nut oil), or animal tissues (as in the case of "rough fat," blubber, fish livers), or caseïn (as in the case of butter), etc., the hydrolysis of the glycerides increases somewhat rapidly, and may reach very high proportions. Thus the so-called bagasse olive oils, *i.e.* oils expressed from exposed olive marc (cp. Vol. II. Chap. XIV. "Olive Oil"), contain as much as 70 per cent of free fatty acids. Palm oil may even undergo complete hydrolysis, and hence consist almost exclusively of fatty acids[2] (cp. also Vol. II. Chap. XIII. "Oil Cakes"). Similar instances are presented by the lower qualities of fish, seal, whale, and cod liver oils (see Vol. II. Chap. XIV.; cp. also chrysalis oil, neats' foot oil, lard grease). In all these cases we can satisfactorily explain the formation of a high proportion of fatty acids by the conjoint action of water and enzymes.[3] It appears, therefore, unnecessary to invoke the action of air and light in order to explain the presence of free fatty acids. Thus it has been frequently observed that the hydrolysis of palm oil continues in the closed casks (*i.e.* in the absence of light and practically also of air) in which it is shipped, and that the liberated glycerol separates out (*Geitel*[1]). Furthermore, *Dieterich*[2] has shown in a very instructive series of experiments that free fatty acids are formed much more rapidly in rough beef fat and pig's fat—still containing animal tissue—than in freshly rendered fat, and that by the addition of 10 per cent of water to both the rough fats and the freshly rendered fats, the rate of hydrolysis was increased considerably. When enzymes are absent, or the conditions are unfavourable for their action, the hydrolysis by moisture alone—which may be aptly termed *auto*-hydrolysis—may require a very long time indeed. Cases of this kind are furnished by the formation of adipocere (see Vol. II. Chap. XIV. "Human Fat") and "bog butter" (*i.e.* butter buried for many centuries in Irish bogs), both of which consist almost entirely of free fatty acids.[3]

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[1] Wigner and Church (*Analyst*, 1888, 17) found in a specimen of melted butter fat taken from an Egyptian tomb (of Queen Hasheps of the 18th dynasty; about 400 or 600 B.C.) 86 per cent of insoluble fatty and 8 per cent of soluble volatile acids. Similarly, Friedel (*Compt. rend.*, 1897 (124), 648) found unchanged triglycerides in the fatty matter buried several thousand years ago in the tombs of Abydos; cp. Berthelot, *Compt. rend.*, 1905 (140), 177; cp. also W. A. Schmidt, *Chem. Zeit.*, 1908, 769.

[2] Adipocere (cp. Vol. II. Chap. XIV. "Human Fat") is another illustration of what may be termed auto-hydrolysis; cp. also Gregory, *Liebig's Annal.* 61 (1847), 362; Wetherill, *Transactions Amer. Philos. Soc.* xi.

[3] Pelouze and Boudet assume the presence of a ferment in palm oil. With regard to the ferment "olease" in olive marc see Vol. II. Chap. XIV. The property of the pancreatic ferment to hydrolyse neutral fats was discovered by Claude Bernard in 1849.

I therefore ascribe the primary cause of rancidity, namely, the formation of free fatty acids, to the action of moisture[4] in the presence of soluble ferments,[5] which act as catalysts or accelerators. It is true that both *Ritsert*[6] and *Reinemann*[7] distinctly stated that ferments have no share in causing rancidity, but their experiments with regard to this point are not exhaustive enough to prove their contention. The different keeping properties of "Neutral Lard No. I" (see Vol. II. Chap. XIV. "Lard") on the one hand, and of "Steam Lard" on the other, are best explained by assuming that in the former case the enzymes are not destroyed completely at the low temperature at which the fat is rendered, whereas in the latter case the steam lard, being rendered at a temperature of 100°-120° C., becomes more immune, and will "keep" under favourable conditions for weeks. In confirmation of this view it may be pointed out that *Zoffmann*[8] has shown that some fungi[9] are not killed at those temperatures at which oils and melted fats are mixed and churned with milk in the manufacture of margarine. More striking still is the observation of *Nicloux*[10] that castor seed

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[1] *Journ. f. prakt. Chem.*, 1897 [55], 417.

[2] *Chem. Rev.*, 1899, 168, 181, 201. Cp. Lewkowitsch, *Jahrbuch d. Chem.* 1899 (ix.), 351. For similar experiments by Pastrovich, see *Monatsh. f. Chem.*, 1904, 355.

[3] Cp. Wigner and Church, *Analyst*, 1880, 17; Radcliffe and Maddocks, *Journ. Soc. Chem. Ind.*, 1907. In this connection it may be noted that Jünnemann (1866) showed that mutton tallow could be hydrolysed by cold running water.

[4] It may be pointed out here that it is very difficult to remove the last traces of moisture from commercial products (see Vol. II. Chap. XIV. "Lard").

[5] Pagenstecher, *Biochem. Zeits.*, 1909 (18), 285, showed that all organs of neat contain lipolytic ferments. Cp. also E. Pennington and S. Hepburn, *Journ. Amer. Chem. Soc.*, 1912 (34), 210.

[6] *Untersuchungen über d. Ranzigwerden d. Fette*, Inaug. Dissert., Berlin, 1890.

[7] *Centralb. f. Bakteriologie, Parasitenkunde und Infektionskrankheiten*, 1900, 131.

[8] *Chem. Rev.*, 1904, 7.

[9] Seeds of a species of Trifolium were heated by *Just* (in 1877) to 120° C. without losing their power of development. *Dixon* showed that several kinds of seeds could withstand a temperature of 105° C. without injury, for several hours (*Nature*, 1909, November, p. 100. Cp. also J. White, *Proc. Roy. Soc.* **81**, 417.

[10] *Contribution à l'étude de la saponification des corps gras*, Paris, 1906, p. 30.

"cytoplasma," which, under suitable conditions, causes rapid hydrolysis of oils and fats, if suspended in oil, may be heated for twenty hours up to a temperature of 100° C. or for fifteen minutes to 110° C. without losing its fat-hydrolysing power. In the presence of water, however, the lipolytic activity is lost completely at a temperature of 55° C.[1] (cp. Vol. III. Chap. XV. "Manufacture of Fatty Acids").

The occurrence of small quantities of free fatty acids, even in refined oils and fats (edible oils and fats), would thus be explained. Yet these oils and fats are by no means rancid. Indeed the presence of the free fatty acids imparts a slight, not unpleasant, flavour; for it is well known that completely neutral oils and fats have an insipid taste. *Heyerdahl*[2] has shown that the addition of cod liver oil free fatty acids (from 2 per cent downwards) to a cod liver oil free from rancidity, did not impart to the oil a rancid character, although it certainly produced a sharp taste. Furthermore, *Lewkowitsch*[3] has shown in the case of a specimen of cacao butter that, although the fat contained free fatty acids, it was not rancid.[4]

Hence, rancidity is not due, as is still widely believed, to the presence of free fatty acids alone; in other words, rancidity must not be considered as coterminous with acidity. The frequent confounding of these two terms is caused by the fact that *acid* oils and fats are frequently rancid as well. It is only when oxygen and light gain access to the acid fats that the conditions favouring the setting in of rancidity are provided. Rancidity is rather due to the direct oxidation of free fatty acids by the oxygen of the air, assisted and intensified by the exposure to light. Oxygen and light must act simultaneously, either of these agents alone being unable to produce rancidity (*Ritsert*); hence, the greater the surface offered to the atmosphere, the more rapidly will they be able to exercise their influence.

I therefore define as rancid those oils and fats, the free fatty acids of which have been acted on by the oxygen of the air, in the presence of light. Similar explanations have been given before, and the only new element I can claim here would consist in ascribing more emphatically than has been done hitherto the initial phase of rancidity, namely, the hydrolysis, to the accelerating action of enzymes.[5] To leave out older statements, *Duclaux*[1] derived from an extended experimental research the conclusion that rancidity is due to slight hydrolysis and the subsequent action of the oxygen in the air assisted by light. *Geitel*[2] has further elaborated this explanation by laying stress on the influence of moisture in the initial stage of hydrolysis.

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[1] These facts are in good agreement with the observations made by Duclaux (*Traité de microbiologie*, 1899, vol. ii. 198) when heating diastases in a dry state, as also with the well-known resistance to high temperatures of spores, such as those of the hay-bacillus and of other low organisms. Cp. Hueppe, *Journ. Chem. Soc.*, 1882, Abst. p. 317; Dunbar, *Centralb. f. Agrikulturchemie*, 1885, 677.

[2] *Journ. Soc. Chem. Ind.*, 1889, 54. Cp. also Besana, *Chem. Zeit.*, 1891, 410, and v. Klecki, *Zeits. f. analyt. Chem.*, 1895, 633.

[3] *Journ. Soc. Chem. Ind.*, 1899, 557.

[4] The observation made by Ballantyne (*Journ. Soc. Chem. Ind.*, 1891, 29) that in several instances (olive oil, cotton seed oil, linseed oil) rancidity set in and continued for some time without the liberation of any free fatty acid whatever, was not corroborated by titration numbers; after a few months, however, liberation of free fatty acids was observed. An explanation may be afforded by assuming that the minute amounts of free fatty acids formed were immediately further broken down with the formation of those substances which cause rancidity.

[5] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1903, 68; *Jahrbuch d. Chemie*, 1897 (7), 368; 1898 (8), 392; 1899 (9), 351; 1900 (10), 382; 1901 (11), 360; 1902 (12), 363; *Conférence, Bull. Soc. Chim. de France*, 1909.

Some authors maintained that rancidity is due to the action of micro-organisms; this view seems to have been supported by the discovery of living micro-organisms[3] in poppy seed oil (*Kirchner*[4]), and by a number of observations made on butter. (Butter, however, containing as it does, in addition to water and enzymes, a considerable amount of organic, non-fatty substances, cannot be placed in the same line with oils and fats which we are considering, for it is butter *fat* and not butter with which we are concerned here.) The same would apply to the destruction of oil in oil cakes.[5] It is quite true that bacteria hydrolyse fats to a great extent (cp. Vol. III. Chap. XVI. composition of "Sewage Fats"), and then further act on the products of hydrolysis, but they accomplish this only when suitable nutriment is offered to them with the fat.[6] In that case the micro-organisms will grow, and as all the necessary conditions are provided, free play is given to those agencies which produce rancidity. It may, however, be left an open question as to whether these changes are due to the direct action of the living organisms, or rather to the action of an enzyme produced by them, much as the alcoholic fermentation of sugar can no longer be ascribed to the action of the living saccharomyces cells, but rather to the zymase produced by them.[7] In confirmation of this view it may be stated that *Duclaux*[8] proved in an investigation on butter *fat* that micro-organisms play no part in producing rancidity, since butter fat, being insoluble in water, does not afford sufficient nutriment to the protoplasma of the cells. (It may be repeated, experiments made on butter[9] do not controvert this.) Similar proof has been given by *Ritsert*,[10] who showed that pure lard is not turned rancid by bacteria, be they aerobic or anaerobic, as the bacteria introduced into the fat die quickly.

Liquid fats—oils—turn rancid more readily than solid fats. This cannot be conditioned by the chemical composition alone, but appears to depend on the manner in which the oils are expressed, the amount of enzymes which are dissolved by the oils during expression, depending to a large extent on the temperature. The fluid (liquid) oils offer a greater surface to the attack of hydrolysing agencies. This agrees with the fact that liquid fats are much more easily hydrolysed in the fermentative process (see Vol. III. Chap. XV.) than are solid fats, such as tallow. Whether fats containing glycerides of lower fatty acids (butter fat, cocoa nut oil) are more liable to become rancid than the fats containing glycerides of the higher fatty acids (cacao butter, tallow, etc.) has not yet been decided experimentally. It may, however, be taken as a general rule that the higher the proportion of insoluble saturated fatty acids, and the lower the percentage of unsaturated glycerides in a fat, the less will be its liability to turn rancid. This rule, however, appears to break down in the case of cocoa nut oil and of Japan wax, which differ greatly in the composition of their constituent glycerides (cp. Vol. II. Chap. XIV.). Further investigation is necessary to elucidate these points.

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[1] *Annales de l'Institut Pasteur*, 1887; *Compt. rend.* (102), 1077.

[2] *Journ. f. prakt. Chem.*, 1897 [55], 448.

[3] For a commercial application of the action of micro-organisms on oils and fats, cp. Meusel, French patent 330,389; English patent 7410, 1903; German patent 149,822.

[4] *Berichte der deutsch. botan. Gesellschaft*, 1888, 101.

[5] Cp. König, Spieckermann, and Bremer, "Die fettverzehrenden Kleinwesen," *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901, iv. 721; E. de Kruyff, *Bullet. Départ. de l'Agric. aux Indes néerl.*, 1907, 9.

[6] Cp. Schmidt, *Flora*, 1891 (74), 300. A. Spieckermann, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, xxiii. 305.

[7] Similarly Piedallu ascribes the fat-hydrolysing action which undoubtedly occurs in the first stages of chamoising skins (see Vol. III. Chap. XVI. "Sod Oil and Dégras") to an "oxydase" secreted by the ascomycetes—Monascus purpureus; cp. also N. L. Soehngen, *Proc. K. Akad. van Wetensch.*, Amsterdam, 1911 (19), 667; Kohshi Ohta, *Biochem. Zeits.*, 1911 (31), 177.

[8] *Annales de l'Institut Pasteur*, 1887; *Compt. rend.* 102, 1077.

[9] Cp. *e.g.* A. Nestrelajew, *Milchwirtschaftl. Zentralb.*, 1910, Heft 1.

[10] *Untersuchungen über das Ranzigwerden der Fette*, Inaug. Dissert., Berlin, 1890.

Whilst it may then be taken as proven that rancidity is due to the simultaneous action of moisture, oxygen, and light, very little is known as to the actual chemical change which the liberated free fatty acids undergo. The observation that rancid fats contain free fatty acids had been made before 1814, and both steam distillation and extraction with alcohol were proposed as means for their removal. Although the number of published observations made since then on this subject is large, no definite conclusions can be drawn therefrom, as they mostly rest on assumptions, or on faulty experimental evidence.[1] Thus several observers, misled by a faulty application of the acetylation test (cp. Chap. VI.), maintained that direct addition of oxygen to the molecule of fatty acids takes place with the formation of hydroxylated acids.[2] *Gröger*,[3] on the contrary, found in a series of experiments extending over four years that the fatty acids isolated from six kinds of fats exposed to the atmosphere, had been broken down into acids of lower molecular weight,[4] and had not merely absorbed oxygen by a process of addition. The same chemist showed that in the further progress of oxidation some acids are oxidised to azelaïc and suberic acids. Other observers suggest that it is principally oleic acid that is set free in rancid oils and fats. *Scala*,[5] who favours this view, isolated from a very rancid olive oil œnanthaldehyde, as also formic, acetic, butyric, and œnanthic acids, and further some soluble acids which he could not identify, and which he assumed to be azelaïc and suberic acids.[6]

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[1] Some of the evidence is based on colour reactions, the rationale of which is entirely unknown. In this connection it may be pointed out that many observers endeavour to find out by chemical means whether a fat is rancid or not, whilst the organoleptic methods (taste and smell) give the answer in the simplest and readiest manner.

[2] Cp. Lewkowitsch, *Analyst*, 1899, 328.

[3] *Journ. Soc. Chem. Ind.*, 1889, 202.

[4] Cp. also Cohn, *Chem. Zeit.*, 1907, 855.

[5] *Staz. Sperim. agric. ital.*, 1897, 30, 613.

[6] In a more recent paper Scala (*Gazz. Chim.*, 1908 (38), i. 307) found in rancid olive oil and lard formic, butyric, caproic, heptylic (heptoic), and nonylic (nonoic) acids, and the following aldehydes: butaldehyde, hexaldehyde (?), heptaldehyde, and nonaldehyde.

However, experiments made by *Thum*[1] with palm oil and rancid olive oil with a view to ascertaining whether palmitic, stearic, and oleic acids are liberated in the same proportion or in a different one from that in which they exist as glycerides in these fats, proved that the ratio between oleic acid and solid fatty acids is the same in their free as in their combined state. This fact was confirmed by *Spaeth* in the case of rancid lard.

The opinion has also been frequently expressed that the bodies characteristic of rancid fats are aldehydes (œnanthaldehyde, *Scala*), and ketones. Hence, the reagents employed usually for the detection of aldehydes have been suggested as a chemical means of differentiating rancid fats from acid fats. *Schmid*[2] stated that rancid fats give off, in a current of steam, volatile substances, which colour yellow a 1 per cent solution of metaphenylenediamine.[3] I have, however, shown[4] that a distinctly rancid cocoa nut oil did not give this reaction.[5] Hence, statements that presence of aldehydic substances in rancid oils and fats is proved beyond doubt must be accepted with reserve. The volatile products from rancid cocoa nut oil give the aldehyde reaction only very faintly. It is true that *Haller* and *Lassieur*[6] found ketones in the volatile products resulting in the refining of cocoa nut oil, but this fact does not prove the formation of these substances from the fatty acids of the cocoa nut oil, as it is quite possible that they are due to the decomposition of the ethereal oil in cocoa nut oil.

Probably *Dakin's*[7] observation that by using mild oxidising agents (such as hydrogen peroxide) all fatty acids from formic up to and including stearic acid can be oxidised at comparatively low temperatures, whereby a series of intermediate products are formed, may throw light on the biological oxidation *in vivo* of the fats and fatty acids (cp. Chap. III. p. 144).

In view of *Dakin's* observations the question has been raised by the present author[8] whether the ketones obtained by *Haller* and *Lassieur* may not be due to the oxidation of capric, lauric, and myristic acids of the cocoa nut oil.

With regard to the glycerol, *Gröger*, being unable to detect free glycerol, adopted the opinion expressed by *Liebig*, and concluded that it must suffer oxidation like the free fatty acids. But considering the

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In *Scala's* opinion the odour and flavour of rancid fats are due, in some degree, to hexaldehyde (?) and butaldehyde, but mainly to heptaldehyde and nonaldehyde. Whilst *Scala* considers all the aldehydes and the corresponding acids to be degradation products of olein and of oleic acid, the absence of formaldehyde leads him to surmise that the formic acid found is due to slow oxidation of glycerol, which can yield formic acid, formaldehyde representing an intermediate stage of oxidation.

[1] *Journ. Soc. Chem. Ind.*, 1891, 70.

[2] *Zeits. f. analyt. Chem.*, 1898, 301.

[3] *Journ. of Biolog. Chem.*, 1908, 227.

[4] *Jahrbuch der Chemie*, 1898 (8), 392; *Journ. Soc. Chem. Ind.*, 1899, 557.

[5] Similar objections were raised against this test by Winkel, *Congrès de chim. et de pharm. Liège*, 1907, section v. 387; cp. also *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 90.

[6] *Compt. rend.*, 1910 (151), 699.

[7] *Journ. of Biolog. Chem.*, 1908, 63, 237.

[8] *Jahrbuch d. Chemie*, 1910, xx. 419. With regard to the opinion of H. Ch. Geelmuyden that acetones are synthesised in the organisms to carbohydrates, cp. *Zeits. f. physiol. Chem.*, 1911 (73), 176.

difficulty which the detection of minute quantities of glycerol offers, and in further consideration of the probability that the hydrolysis of the rancid fats examined by him had only proceeded to the formation of di- and mono-glycerides (cp. Chap. II. p. 72), his view cannot be accepted as proven.[1] Against *Gröger's* opinion we have the well-ascertained fact that glycerol in dilute as well as in concentrated solutions will " keep " indefinitely, without becoming " rancid."

In the present state of our knowledge we are still unable to discern rancid oils and fats by chemical means. There is, however, no need for chemical reactions, as we can rely on the taste and smell as the best means of ascertaining whether a fat is rancid or not.

Some isolated observations regarding the chemical change suffered by rancid fats are given in the following table, published by *Lewkowitsch* :[2]—

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[1] Friedel (*Compt. rend.*, 1897 (124), 648) also concluded from the examination of fat found in the tombs of Abydos that glycerol was oxidised, without, however, adducing any proof for his statement.

[2] *Analyst*, 1899, 327 ; cp. also *Journ. Soc. Chem. Ind.*, 1899, 557 ; Sherman and Falk, *Journ. Amer. Chem. Soc.*, 1903, 711 ; 1905, 680.

[TABLE

	Fresh.								After Exposure.								
	Original Oil or Fat.		Acetylated Oil or Fat.						Original Oil or Fat.		Acetylated Oil or Fat.						
	I.	II.	III.	IV.	V.		VI.	VII.	VIII.	IX.	X.	XI.	XII.		XIII.	XIV.	XV.
Oil or Fat.	Saponification Value.	Total Volatile Fatty Acids per Gram in terms of Milligrams KOH.	Saponification Value.	Insoluble Acids + Unsaponifiable.	Apparent Acetyl Value.		True Acetyl Value.	Difference, III.-I.	Saponification Value.	Total Volatile Fatty Acids per Gram in terms of Milligrams KOH.	Saponification Value.	Insoluble Acids + Unsaponifiable.	Apparent Acetyl Value.		True Acetyl Value.	Difference, X.-VIII.	Difference, XIII.-VI.
					Distillation Process.	Filtration Process.							Distillation Process.	Filtration Process.			
Cotton seed.	...	0·1	200·2	95·7	...	7·4 8·0	7·6	...	193·0	2·1	201·8	94·0	8·3	10·1	7·1	8·8	−0·5
Curcas . .	193·2	...	...	95·5	7·5	...	...	...	194·2	1·5	200·4	...	...	9·44	7·94	6·2	...
Castor . .	179·0	0·0	304·1	...	...	146·9	146·9	125·1	180·2	1·8	304·6	...	...	146·6	144·8	124·4	...
Cod liver .	186·45	3·6	189·15	...	4·75	...	1·15	2·7	192·7	8·7	199·7	...	...	19·15	10·45	7·0	+9·3
Cacao butter	192·6	0·81	...	...	2·86	2·71	1·97	...	193·1	0·49	...	...	5·0	4·8	4·41	...	+2·44
Tallow . .	196·2	1·55	200·5	94·75	6·1	6·1	4·55	4·3	200·0	2·9	210·7	93·2	14·5	12·7	10·7	10·7	+6·15
"Premier jus"	...	0·58	199·6	...	...	3·3	2·72	...	199·8	2·3	206·2	93·6	11·2	8·2	8·9	6·4	+6·18

It will be gathered from this table that rancid fats exhibit higher acetyl numbers than do the same fats in the fresh state. Yet the number of experiments made hitherto is too small to afford conclusive evidence in favour of my opinion that the "acetyl value" indicates rancidity in a more reliable manner than do the doubtful colour reactions proposed up to the present. A further chemical difference between fresh and rancid fats may be found in the difference of the heats of combustion. Rancid fats yield considerably lower values than do fresh fats (*Stohmann and Langbein* [1]). This is explained by the higher proportion of oxygen contained in rancid fats.

If air, or in order to accelerate the action, *oxygen*, be blown through fatty oils at the temperature of boiling water, oxidation takes place. So much heat is thereby evolved that the oxidation process continues without further heating. On this reaction is based the industry of "blown oils" (Vol. III. Chap. XV.). The most notable change produced by the action of oxygen is an increase in density ("Thickened Oils"). The oils thus obtained simulate castor oil in their density and viscosity, but differ from it in that they are soluble in petroleum ether ("Soluble Castor Oils"). The similarity to castor oil, as also the high acetyl values of the blown oils, led to the opinion that glycerides of hydroxylated acids are formed, but it should be noted that the fatty acids actually produced differ from the castor oil fatty acids (see Chap. VIII. "Oxidised Acids," and Vol. III. Chap. XV.). Fatty oils belonging to the class of *semi-drying oils* lend themselves specially to the manufacture of "blown oils."

In the case of *drying oils* the oxidation process proceeds much further, finally yielding jelly-like or even solid elastic masses. This reaction is made use of in the linoleum industry (cp. Vol. III. Chap. XV.). If the temperature of the oils during the blowing operation be raised still higher, considerable quantities of volatile products are formed. In the case of castor oil [2] there were found in the condensed products normal caproic and normal heptylic acids, œnanthaldehyde, iso-heptylalcohol, and iso-octylalcohol. In the case of rape and linseed oils also high-boiling alcohols and aldehydes were identified among the volatilised substances. The non-drying oils are less readily attacked, and solid fats only suffer a change if heated to a higher temperature than 100° C. (cp. Chap. VII. "Oxygen Absorption").

For further information on this subject cp. Chapter VII. "Oxygen Absorption Test," and Vol. III. Chap. XV. "Oxidised Oils."

Behaviour with Reagents

Hydrogen Peroxide.—The action of hydrogen peroxide on fats is of greater importance to the physiological chemist than to the technical chemist. From the experiments of *Dakin* (recorded below), it appears that the reagent chiefly attacks the fatty acid constituent of the oils and fats (after they have become hydrolysed), although hydrogen peroxide is not without action on glycerol (see below). The oxidation of chicken fat has been made the subject of a study by J. S. Hepburn.[1]

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[1] *Journ. f. prakt. Chem.* 42, 361.

[2] Nördlinger, German patent 167,137.

Ozone.—Ozone has no action on the glycerides of saturated fatty acids. The glycerides of unsaturated fatty acids are easily acted upon by ozone. According to *Molinari* and his collaborators, *Soncini and Fenaroli*,[2] one molecule of ozone is absorbed by each pair of doubly-linked carbon atoms (much in the same manner as two atoms of iodine are absorbed by each pair of doubly linked carbon atoms). The new substances thus obtained are comprised under the term fatty "ozonides," and the quantity of ozone absorbed can be determined by the increase in weight which the oils and fats acquire.[3] According to *Harries* [4] and his collaborators, *Thieme* and *Türk*,[5] "perozonides" appear to be formed first (cp. below, Chap. III. "II. Acids of the Oleic Series" and "Oleic Acid"), which are readily converted into stable ozonides.

Hydrogen gas, under ordinary conditions or under pressure, or even if evolved in *statu nascendi*, either electrolytically or by means of sodium amalgam, has no action on the glycerides of higher unsaturated fatty acids. Statements have been made by *Fokin* [6] that natural oils can be reduced by electrolytic hydrogen under the same conditions which hold good for the reduction of oleic acid (cp. Chap. III., and Vol. III. Chap. XV. "Conversion of Oleic Acid into Candle Material"), but no definite products appear to have been isolated.

Sabatier and Senderens,[7] however, furnished by their general method of reducing unsaturated organic substances by means of hydrogen, *in the presence of finely divided metals*, especially of finely divided nickel, an easy means of converting the glycerides of unsaturated fatty acids into practically completely saturated glycerides. Thus linseed oil, whale oil, cotton seed oil, sesamé oil, etc., can be reduced to hard tallow-like substances which practically absorb no iodine. The reduction of unsaturated glycerides by means of hydrogen has also been effected *in the cold*, by *Paal and Roth*,[8] with the aid of colloidal palladium (*Paal and Amberger* [9]) as a contact substance. They were thus able to reduce olive oil, castor oil, and cod liver oil (cp. Vol. II. Chap. XIV. "Olive Oil," "Castor Oil," "Cod Liver Oil") to practically saturated substances. More recently the reduction has been effected by means of finely divided metallic palladium and platinum or their hydroxides or salts.[1] *Paal* and his collaborators used as the protective colloid for their experiments lysalbic and (or) protalbic[2] acid (from albumen); more recently *C. Kelber and A. Schwarz*[3] proposed as a more readily obtainable colloid—glutin.

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[1] *Journ. Amer. Chem. Soc.*, 1912, 210.

[2] *Ann. d. Soc. Chim. di Milano*, 1903, ix. p. 507; 1905, xi. p. 89; 1906, xii. Fascic. i., ii., iii., and iv.; *Berichte*, 1908, S. 2735; *Gazz. Chim.* 36; ii. 292.

[3] The saponification values of triolein ozonide and of the ozonide obtained from olive oil are given by Molinari and Fenaroli (*Berichte*, 1908, 2789) as 276·5 and 223·7 respectively. (Theory requires, however, for triolein ozonide 163·7. J. L.)

[4] *Liebig's Annal.*, 343, 311; 374 (1910), 288; *Berichte*, 1912, 936.

[5] *Berichte*, 1906, 3728; 3732.

[6] *Zeit. f. Elektrochemie*, 1906 (12), 749; cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1908, 489.

[7] Cp. "Nouvelles méthodes générales d'Hydrogénation," *Annal. de Chim. et de Phys.*, 1905 (iv.) Mars-Avril. Cp. also P. Sabatier, "Hydrogénation et déshydrogénation par catalyse," *Berichte*, 1911, 1984.

[8] *Berichte*, 1908, 2283; 1909, 1541.

[9] *Berichte*, 1904, 124; 1905, 1398.

The reduction of commercial oils and fats by the above indicated processes has acquired technical importance, and a large number of patents have been taken out during the last few years for the "hardening" of oils (see "Hydrogenated Fats," "Hardened Fats," Vol. III. Chap. XV.), and even of lecithin, "Hydrolecithin."[4] *P. Breteau*[5] recommends for purposes of hydrogenation metallic calcium in a solution of absolute alcohol.

The action of hydrogen on natural oils and fats extends also to the concomitant substances, such as sterols and chromogenetic bodies. Further information on this latter point will be found under the heading of individual Oils and Fats, in Vol. II. Chap. XIV.

Chlorine.—Chlorine acts on oils and fats with evolution of hydrochloric acid, glycerides of chlorinated fatty acids being formed. At the same time, if unsaturated glycerides are present, chloro-addition products are obtained. Hitherto it has not been possible to moderate the action of chlorine to such an extent that chloro-addition products are obtained exclusively. Attempts are being made at present to find applications for chlorinated oils and fats in the arts[6] (see Vol. III. Chap. XV. "Chlorinated Oils and Fats").

Bromine.—Bromine acts in a manner similar to chlorine, although much less violently, so that it is possible to limit the reaction in the case of unsaturated glycerides to such an extent that bromo-addition products only are obtained. Hence it is possible to prepare on a practical scale brominated oils and fats. Such products are recommended for pharmaceutical purposes (see Vol. III. Chap. XV. "Brominated Oils and Fats").

Iodine is but slowly absorbed when mixed with an oil or fat, but does not yield substitution products. The assimilating power of unsaturated oils or fats for iodine varies with the chemical constitution of their glycerides and also with the temperature, but never reaches that theoretical amount which is indicated by the iodine value (cp. Chap. VI.). (Hence, such statements as *Focke's*,[7] that liver oils dissolve as much as 20 per cent, and neat's foot oil 33 per cent of iodine, must be ignored.) The absorption of iodine in oils and fats at the ordinary temperature is assisted by the addition of a small quantity of potassium (or sodium) iodide. Complete saturation of the unsaturated glycerides with *halogens* can be effected in the cold readily if an alcoholic solution of iodine and mercury bichloride or a solution of iodine monochloride or iodine monobromide in glacial acetic acid is allowed to act on a dilute solution of the oils or fats (see Chap. VI. "Iodine Value"). The glycerides of the unsaturated acids absorb in that case one molecule of iodine chloride or iodine monobromide for each pair of doubly-linked carbon atoms, with the formation of saturated compounds. This has been proved by the actual isolation of the chloro-iodo-addition compound of oleodistearin (*Henriques and Künne*[1]). By heating the chloro-iodo-compound with a base (chinoline), the halogens are eliminated with the regeneration of the original glycerides. On this action is based one of the most important analytical operations practised in the examination of oils and fats, viz., the determination of the iodine value (see Chap. VI.). The action of halogens has found technical application in the preparation of iodo-bromo-fats (cp. Vol. III. Chap. XV.) for pharmaceutical purposes.

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[1] Cp. P. Breteau, "Hydrogénation au moyen du palladium précipité et de l'hypophosphite," *Bull. Soc. Chim. de France*, 1911, 515. "Hydrogénation au moyen du nickel et de l'hypophosphite de sodium," *ibid.* 518.

[2] For the commercial preparation cp. German patent 248,525, Kalle & Co.

[3] *Berichte*, 1912, 1947.

[4] J. D. Riedel, A.-G. Method of preparing Hydrolecithin, German patent; cp. Paal and Oehme, *Berichte*, 1913, 1297.

[5] *Journ. de pharm. et de chim.*, 1911, 580.

[6] Electrolytic Alkali Co., C. C. Connor and J. W. Stubbs, English patent 741, 1908; C. F. Böhringer & Sons, German patent 248,779.

[7] *Pharm. Zeit.*, 1896, 616.

Sulphur chloride acts energetically on fats (cp. Chap. VII.). The reaction appears to consist in an absorption of the elements of sulphur chloride, much as iodine chloride is absorbed by unsaturated carbon atoms. The action of sulphur chloride would therefore appear to consist in the conversion of unsaturated glycerides into saturated compounds. This reaction finds technical application in the manufacture of vulcanised oils (cp. Vol. III. Chap. XV.).

Sulphur has no chemical action on oils and fats in the cold. At higher temperatures, however, from 120°-160° C., all oils assimilate sulphur, and it would appear that the sulphur is absorbed much in the same manner as oxygen is absorbed by oils. *Altschul*[2] demonstrated that stearic acid is hardly acted upon by sulphur at a temperature of about 130° C., whereas oleic acid when treated with 10 per cent of sulphur at 130°-150° C. absorbs sulphur without any evolution of sulphuretted hydrogen. In a similar manner fatty oils (because containing glycerides of the unsaturated fatty acids), notably linseed oil, castor oil, rape oil, cotton seed oil, and marine animal oils, absorb sulphur at 120°-160° C. On cooling, sulphur does not separate out; on saponifying the sulphurised oils in the cold, sulphurised fatty acids are obtained, whilst very little sulphuretted hydrogen is evolved.[3] On heating the sulphurised fatty acids to 130°-200° C., however, sulphuretted hydrogen escapes in large quantities, and substitution of hydrogen in the molecule of the fatty substance by sulphur seems to take place. It is doubtful whether thiozonides[4] are formed. The action of sulphur on oils is made use of in the manufacture of vulcanised oils (see Vol. III. Chap. XV.).

Phosphorus has no chemical action in the cold. When heated at about 220° C. with vegetable drying oils, it is stated to cause polymerisation of these oils, especially in the presence of phenol.[5] This reaction stands in need of further elucidation.

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[1] *Berichte*, 1899, 387; cp. also Holde, *ibid.*, 1902, 4306.
[2] *Journ. Soc. Chem. Ind.*, 1896, 282.
[3] Henriques, *Journ. Soc. Chem. Ind.*, 1896, 282.
[4] Erdmann, *Liebig's Annal.* 362 (1908), 170.
[5] K. Winkler, German patent 252,139.

Carbonic acid dissolves to some extent in oils, especially under pressure. At atmospheric pressure the dissolved gas escapes with effervescence (cp. Vol. III. Chap. XV. "Effervescent Fats"). Lard also absorbs carbonic acid to some extent, and acquires thereby a tallow-like taste. With regard to the part which carbonic acid plays in the natural hydrolysis of oils and fats in seeds, cp. above, pp. 42, 43.

Concentrated nitric acid attacks oils and fats, acting on them violently, with copious evolution of red fumes. Hot dilute nitric acid oxidises oils and fats gradually. *Fahrion*[1] concluded from some experiments that all glycerides of unsaturated acids when acted upon by nitric acid give rise to the formation of hydroxylated acids, which on further treatment with nitric acid are said to be converted into nitro-derivatives of hydroxylated acids. These statements stand greatly in need of confirmation; it appears, however, that "oxidised" acids (Chap. VIII.) were formed.[2]

Fuming nitric acid, in presence of concentrated sulphuric acid, reacts with linseed oil and castor oil to form "nitrated" oils, the nature of which has not yet been investigated, although they have found technical application (cp. Vol. III. Chap. XV. "Nitrated Oils").

Nitrous Acid.—On treatment with nitrous acid, the non-drying oils become solid, or acquire the consistence of butter according to the proportion of triolein (trierucin, etc.) they contain, triolein (trierucin, etc.) being converted into the solid isomeride trielaïdin (tribrassidin, etc.) (cp. Chap. VII.). The vegetable drying oils, on the other hand, remain liquid under similar treatment. According to *Lidoff*,[3] their specific gravity, as also their viscosity and saponification values, increase, whereas their iodine values and the proportion of insoluble fatty acids decrease. According to the same author, all oils after treatment with nitrous acid contain nitrogen, varying in amount from 1 to 2·5 per cent. These nitrogenous substances may be reduced, yielding new compounds, which are stated to contain probably the NH_2 group. The free unsaturated acids yield no such compounds. These statements stand in need of confirmation.[4] The fish, liver, and blubber oils behave with nitrous acid like the vegetable drying oils.

Concentrated Sulphuric Acid.—On mixing concentrated sulphuric acid with oils and fats at the ordinary temperature, a rise of temperature (*Maumené's* test, Chap. VII.) and evolution of sulphurous acid become noticeable. If an oil containing chiefly glycerides of *unsaturated fatty acids* be mixed with the acid very gradually, and at a low temperature, glycerides of a complex constitution are formed. Thus, on treating olive oil with concentrated sulphuric acid a compound was obtained which may be regarded (*Geitel*[5]) as a mixed glyceride of oleic acid, stearic acid hydrogen sulphate, and hydroxystearic acid,[5] having the formula

$$C_3H_5[O.C_{18}H_{33}O].[O.C_{18}H_{34}(SO_4H).O].[O.C._{18}H_{34}(OH)O].$$

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[1] *Zeits. f. angew. Chem.*, 1891, 74.

[2] Cp. also English patent 3716, 1900 (S. von Graeve and A. Reinecken)

[3] *Journ. Chem. Soc.*, 1893, Abstr. ii. 559.

[4] Cp. Lewkowitsch, *Jahrb. d. Chemie*, 1896 (6), 378.

[5] *Journ. f. prakt. Chem.*, 1888 [53], 218.

This product is very unstable in the presence of water. On boiling with water it is rapidly decomposed into compounds which form a complete emulsion with the fat and water (cp. Chap. II., and Vol. III. Chap. XV. " Sulphuric Acid Saponification "). This reaction is made use of in the manufacture of Turkey-red oils (Vol. III. Chap. XV.).

In a study of the action of concentrated sulphuric acid on laurin —*i.e.* a saturated glyceride—*van Eldik Thieme*[1] showed that in the first instance there is most likely formed an addition product which, on the addition of a further quantity of sulphuric acid, induces the " acid saponification process " (see Chap. II., and Vol. III. Chap. XV.), in which, apparently, the sulpho group, SO_3H, enters into the molecule of laurin and produces free lauric acid, which in turn forms an addition product with sulphuric acid. This reaction only takes place at a low temperature and by using about 52 molecules of a 100 per cent sulphuric acid. *Grün and Corelli* also studied the action of sulphuric acid on a saturated glyceride with tristearin. Since the validity of their conclusions has been questioned by *van Eldik Thieme*, the reader must be referred to the original paper.[2]

The action of concentrated sulphuric acid on natural oils and fats, representing as they do a mixture of glycerides of saturated and unsaturated acids, will obviously lie midway between the two typical examples chosen above for unsaturated and saturated glycerides respectively.

At a temperature exceeding 100° C., concentrated sulphuric acid reacts energetically with all oils and fats, partly carbonising them, but chiefly converting them into sulpho-compounds. On steaming, the latter are hydrolysed to glycerol and sulpho-fatty acids, which in turn are decomposed into sulphuric acid and fatty acids. On this reaction is based the " acid saponification " process employed in the candle industry (see Chap. II., and Vol. III. Chap. XV.).

Dilute sulphuric acid, even at temperatures of 100° C., does not act on oils and fats (*Lewkowitsch*[3]).

A dilute solution of *sulpho-aromatic compounds* (*Twitchell's reagent*) readily effects hydrolysis (cp. Chapter II.) of the glycerides.

Hydrochloric acid exercises a very slow action at the ordinary temperature (see Chap. II.); at higher temperatures it behaves as a catalytic agent, and accelerates considerably the hydrolysis of oils and fats.

Caustic alkalis, and less readily *alkaline earths*, if treated with oils and fats in contact with water, act in the first instance as catalysts and readily induce the hydrolysis of the glycerides (see Chap. II.). The free fatty acids formed combine immediately with the caustic alkalis and alkaline earths to form soaps. On this reaction are based some of the most important processes practised in the candle- and soap-making industries.

[1] *Journ. f. prakt. Chem.*, 1912 (85), 284.

[2] *Zeits. f. angew. Chem.*, 1912, 668.

[3] *Journ. Soc. Chem. Ind.*, 1903, 63.

Ammonia hydrolyses oils and fats to some extent if acting under pressure[1] (see Vol. III. Chap. XV.). Alcoholic ammonia on prolonged standing in the cold with oils and fats yields amides (*Rowney*[2]).

Aromatic bases, such as aniline, etc., react similarly with oils and fats on being heated under pressure to 210° C. In the case of aniline, the reaction was stated to take place according to the following equation[3]:—

$$C_3H_5(OR)_3+3C_6H_5.NH_2=C_3H_5(OH)_3+3C_6H_5.NH.R$$

(cp. Vol. III. Chap. XV.), and the yield of glycerol recovered was stated to be nearly 90 per cent. *Kulka*[4] showed that the process is entirely unworkable on a practical scale. *Quensell*[5] hydrolysed the (synthetically prepared) glycerides of stearolic and behenolic acids with aniline; the yield of the anilide of fatty acids was, however, not stated.

If hydroxylamine be used, hydroxam derivatives[6] of the fatty acids are obtained, together with glycerol, as is exemplified by the following equation:—

$$C_3H_5(OR)_3+3NH_2.OH=C_3H_5(OH)_3+3R.(N.OH)OH.$$

The chemical changes involved by the action of acids and alkalis in the presence of water are of the greatest importance, both for the chemistry of oils and fats and in the industries connected therewith; they will, therefore, be treated specially and explicitly from a scientific point of view in the following chapter, and from a technical point of view in Vol. III. Chap. XV.

Oils and fats dissolve sulphur and phosphorus (see Chap. IV., and Vol. III. Chap. XV. "Sulphurised Oils," "Phosphorised Oils") at the ordinary temperature[7] to a slight extent.[8] They also dissolve small quantities of soaps; the solubility of the latter is considerably increased by the presence of ether and petroleum ether (cp. Chap. VI. "Unsaponifiable Matter").

II. WAXES (LIQUID AND SOLID)

1. Chemical Constitution of Waxes. Preparation and Properties of Pure Waxes

The most essential point of difference between fats and waxes has been explained already. Fats are the glycyl esters of the higher fatty acids, whilst the waxes proper must be considered as esters formed by the combination of mono- or dihydric alcohols with higher fatty acids. Thus cetin, or cetyl palmitate, is obtained from cetyl alcohol and palmitic acid by abstraction of water, according to the following equation—

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[1] Although this method has been patented frequently, new patents are still being taken out; cp. Barbé, Garelli, and de Paoli, French patent 372,341, and First Addition No. 9255; Krebitz, German patent 189,685; French patent 369,523; English patent 4092, 1905.

[2] *Jahresberichte*, 1855, 531.

[3] Liebreich, German patents 136,274, 136,917; French patent 322,026; English patent 12,957, 1902.

[4] *Chem. Revue*, 1909, 30.

[5] *Inaug. Dissert.*, Berlin, 1909, 13.

[6] Morelli, *Atti R. Accad. dei Lincei*, 1908, 17, ii. 74.

[7] At the temperatures above 180° C. sulphur interacts with fats (cp. p. 61).

[8] On the solubility of indigo in oils and fats, cp. *Journ. Soc. Chem. Ind.*, 1895, 1027; and on the solubility of coffeïn cp. *Zeits. f. angew. Chem.*, 1909, 1838. For the preparation of solutions of colouring matters in oils and fats cp. German patent 198,278 and addition to it, German patent 213,172, *Chem. Fabrik Flörsheim*.

$$\mathrm{C_{16}H_{33}.OH+C_{15}H_{31}.CO.OH=C_{16}H_{33}.O.CO.C_{15}H_{31}+H_2O}.$$

Therefore, whilst all fats have one common basic constituent—namely, the trihydric alcohol: glycerol—the waxes are characterised by their basic constituents being monohydric and dihydric alcohols. The alcohols hitherto identified in waxes belong both to the aliphatic and cyclic series; the former are represented by alcohols of the ethane, allylic, and glycolic series, the latter by the sterols. Amongst the solid fatty acids, none found hitherto has a lower number of carbon atoms than myristic acid. The fatty acids of wool wax are remarkable for the ease with which they are converted into lactones.[1] The nature of the liquid fatty acids in waxes has not yet been ascertained fully.

The following pure "waxes" have been isolated from natural waxes, or have been prepared synthetically by the usual methods employed for the preparation of simple esters:[2]—

Cetyl Palmitate, Cetin, $\mathrm{C_{16}H_{33}.O.CO.C_{15}H_{31}}$, the chief constituent of spermaceti, is prepared by repeatedly crystallising spermaceti from ether. Cetin forms white crystals, melting at 55° C., easily soluble in boiling alcohol, but nearly insoluble in cold alcohol. In a vacuum, cetin can be distilled unchanged. When distilled under ordinary pressure, or even under a pressure of 300 to 400 mm., it is split into palmitic acid and the hydrocarbon hexadecylene (cetene), as is indicated by the following equation—

$$\mathrm{C_{16}H_{33}.O.CO.C_{15}H_{31}=C_{16}H_{32}O_2+C_{16}H_{32}}.$$

Octodecyl Palmitate, $\mathrm{C_{18}H_{37}.O.CO.C_{15}H_{31}}$, forms crystals melting at 59° C.

Ceryl Palmitate, $\mathrm{C_{26}H_{53}.O.CO.C_{15}H_{31}}$, the chief constituent of opium wax, crystallises from boiling alcohol in small prisms, melting at 79° C., and solidifying at 76° C.

Myricyl Palmitate, Myricin, $\mathrm{C_{30}H_{61}.O.CO.C_{15}H_{31}}$, the chief constituent of that portion of beeswax which is insoluble in alcohol, forms feather-like crystals melting at 72° C.

Cetyl Stearate, $\mathrm{C_{16}H_{33}.O.CO.C_{17}H_{35}}$, forms large scales resembling those of spermaceti. Cetyl stearate melts at 55°-60° C.; it distils at 360° C. without perceptible decomposition. It is readily soluble in ether, chloroform, carbon bisulphide, and in boiling alcohol.

Ceryl Cerotate, $\mathrm{C_{26}H_{53}.O.CO.C_{25}H_{51}}$, occurs in Chinese wax, which consists almost exclusively of this ester. It has also been found in opium wax, and very likely occurs in wool fat. Ceryl cerotate forms snow-white, lustrous scales (from chloroform) melting at 82·5° C.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 132; 1896, 14.

[2] It may be pointed out that by fusing together cholesterol with fatty acids (palmitic, stearic, oleic), no esters are formed. From the melt either the original substances are obtained or mechanical mixtures thereof. If, however, carbonic acid is passed through the melted mass at temperatures above 250° C., so as to carry away water, then esters are formed (as in Scheij's method).—J. R. Partington, *Journ. Chem. Soc.*, 1911, 313.

Cocceryl Coccerate, Coccerin, $C_{30}H_{60}(O.C_{31}H_{61}O_2)_2$, has been obtained from the cochineal wax (*Liebermann*[1]) in the form of nacreous, thin laminæ (from benzene) melting at 106° C. Coccerin is nearly insoluble in cold alcohol and ether, and dissolves with great difficulty in cold benzene and glacial acetic acid.

Cholesteryl Palmitate, $C_{27}H_{45}.O.CO.C_{15}H_{31}$, occurs in blood-serum,[2] and in the human epidermis;[3] it forms snow-white plates melting at 77°-78° C. (*Hürthle*[2]), 79° (*Windaus*[4]), or long needles of silky lustre melting at 77° C. (*Herbig*[5]). It is prepared synthetically by *Berthelot's* method (cp. cholesteryl stearate) (*Hürthle*) or by passing a current of dry hydrochloric acid through a mixture of 30 grms. of cholesterol and 50 grms. of palmitic acid at a temperature of 124° C. (*Herbig*[5]).

Cholesteryl Stearate, $C_{27}H_{45}.O.CO.C_{17}H_{35}$, has been prepared synthetically by heating one part of cholesterol with 8-10 parts of stearic acid to a temperature of 200° C. (*Berthelot*). It has been stated to occur in wool wax conjointly with isocholesteryl stearate (cp. Vol. II. Chap. XIV. " Wool Wax "). It crystallises in small needles melting at 82° C., is nearly insoluble in alcohol, and only slightly soluble in ether. At 37° C. cholesteryl stearate is capable of holding in solution :—olive oil, 3·37 per cent; castor oil, 0·26 per cent; oleic acid, 4·11 per cent; ricinoleic acid, 0·33 per cent.[6]

Isocholesteryl Stearate, $C_{27}H_{45}.O.CO.C_{17}H_{35}$, has also been obtained by synthetical methods. It crystallises in fine needles melting at 72° C., and is but very slightly soluble in boiling alcohol.

Cholesteryl Oleate, $C_{27}H_{45}.O.CO.C_{17}H_{33}$, has been found conjointly with the palmitate in blood-serum. It crystallises in long, thin needles melting at 42° C.; it is soluble in ether, chloroform, and benzene, but only sparingly so in alcohol; its specific rotation is $[\alpha]_D = -18° 48'$.[7]

Cholesteryl Cerotate, $C_{27}H_{45}.O.CO.C_{25}H_{51}$, is prepared by passing a current of dry hydrochloric acid through a mixture of cholesterol and cerotic acid at 145° C. for two hours; after repeated crystallisation from petroleum ether it forms a powdery non-crystalline mass (*Herbig*[5]) melting at 85·5° C.

Melissyl Melissate (*Myricyl Melissate*), $C_{30}H_{61}.O.CO.C_{29}H_{59}$, occurs in gum lac (*Gascaro*) and on the bark of *Iatropha Curcas* (see " Curcas Wax," Vol. II. Chap. XIV.); it melts at 92° C. The statement made by *Kissling*,[8] that melissyl melissate occurs in tobacco, has been refuted by *Thorpe and Holmes*.[9] Hence *Kissling's* note as to the occurrence of this wax in hay also stands in need of confirmation.

For other esters of cholesterol and its congeners see Chap. III.

[1] *Berichte*, 1885, 1975.

[2] Hürthle, *Journ. Chem. Soc.*, 1896, Abstr. i. 485.

[3] Salkowski, *Biochem. Zeits.*, 1910 (23), 361.

[4] Hoppe-Seyler's *Zeits. f. phys. Chem.* 65 (1910), 117.

[5] *Zeits. f. öffentl. Chem.*, 1898 (4), 227.

[6] Filehne, *Zeit. f. die gesamte Biochemie*, 1907, 304.

[7] The preparation of solutions of cholesteryl oleate in fatty acid esters and in natural oils and fats has been patented by the Farbenfabriken vorm Fr. Bayer & Co., German patent 236,080.

[8] *Chem. Zeit.*, 1901, 684.

[9] *Journ. Chem. Soc.*, 1901, 982.

2. Properties of Natural Waxes

Liquid waxes have hitherto been found only in animals, and are represented by two " species " of waxes which are so nearly related to each other that up to the present it has been impossible to distinguish them by chemical means alone. These liquid waxes are most probably compounds formed by the union of unsaturated alcohols, of the series $C_nH_{2n}O$, with unsaturated fatty acids.[1] In the fresh state they are practically neutral compounds, hence they contain only small proportions of free fatty acids; they do not emit the odour of acroleïn on heating, as glycerol is absent.[2] In their physical properties the liquid waxes much resemble fatty oils. They also behave similarly to solvents. Much as animal oils and fats of one and the same species vary with the race and breed, food, etc., so vary also animal waxes, especially beeswaxes (see " Beeswax," Vol. II. Chap. XV.).

Liquid waxes are readily distinguished from fatty oils by their lower specific gravities, which vary from 0·875 to 0·881.

Solid waxes, although very widely distributed as secretions of both vegetable and animal organisms, occur in much smaller quantities than do oils and fats. The waxes secreted by the lowest organism, such as bacilli and algæ, have not yet been fully investigated, although the former is now prepared commercially (cp. Vol. II. Chap. XIV.). The wax secreted by algæ in the earlier history of the earth is considered by *Kraemer* to be the mother-substance of petroleum, or at least of some varieties (" species " [3]) of petroleum,[4] a view to which *Höfer* strongly objects. The wax-like substances occurring in lignite and peat would also appear to belong to the vegetable waxes; on account of the commercial importance which the decomposition products of these substances possess they will be considered under " Candle Manufacture " (Vol. III. Chap. XV.).

The solid waxes differ in certain respects from the fats with regard to their behaviour to solvents. Some are completely soluble in ether, whereas others are only partly soluble. They also differ in their solubility as regards boiling alcohol. In their liquid state they leave a grease spot on paper like fats. They do not turn rancid on keeping, owing to the stability of the esters (as also of their fatty acids). The fatty acids belong preponderantly to the saturated series. The following liquid acids—oleic, linolic, and linolenic—have been stated to occur in flax wax (see Vol. III. Chap. XV.). On destructive distillation the esters of the solid waxes are readily converted into hydrocarbons. According to *Redtenbacher*,[5] no sebacic acid is found in the products of distillation.

Spermaceti and insect wax consist practically of pure esters (cetylpalmitate and cerylcerotate respectively), and in their fresh state are devoid of free fatty acids, free alcohols, and hydrocarbons. They thus approximate in their chemical composition more closely to the liquid waxes than to the other solid waxes.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 135.

[2] Cp., however, "Sperm Oil," Vol. II. Chap. XIV.

[3] Cp. *Jahrbuch der Chemie*, 1900, x. 391.

[4] *Ibid.*, 1907, xvii. 416.

[5] *Liebig's Annal.*, 1840 (35), 190.

Carnaüba wax, wool wax, and beeswax amongst the solid waxes have not yet been examined so thoroughly that definite statements as to their composition can be made. They consist to a great extent of esters, but contain also considerable quantities of free fatty acids and free alcohols (in the case of carnaüba wax most likely also lactones). Notable amounts of hydrocarbons are found in carnaüba wax and in beeswax.

Whereas in the case of oils and fats, the occurrence of free fatty acids must be considered as an indication that hydrolysis has taken place, the same cannot be said with certainty of the waxes; at any rate not in the present state of our knowledge. Perhaps the conjecture is permissible that the occurrence of free fatty acids is due to a secondary action, if we bear in mind that in those waxes which contain free fatty acids, free alcohols are present simultaneously. Some vegetable waxes, *e.g.* Raphia wax, appear to consist entirely of alcohols. In the case of fats the free "alcohol" escapes detection, as glycerol is very easily soluble in water.

The flash points of beeswax and carnaüba wax are lower than those of oils and fats (beeswax 244°-250° C.; carnaüba wax 310° C.) (*Stoeber*[1]). This is perhaps due to the volatilisation of the free alcohols; at any rate, in the case of wool wax, the author was able to prove that free alcohols volatilised at a comparatively low temperature.

It cannot yet be stated with certainty whether the vegetable waxes differ from animal waxes by presence of phytosterol. Wool wax is pre-eminently characterised by containing a very large proportion of cholesterol and isocholesterol. *Berg*[2] is of the opinion that beeswax contains cholesterol, but this must be accepted with reserve as the proof for the presence of cholesterol rests on doubtful colour reactions.

The presence of phytosterol has so far been proved in the vegetable flax wax.

Although insoluble in water, the solid waxes have the property of forming emulsions with water, so much so that large quantities of water can be incorporated with them (Vol. II. Chap. XIV. and Vol. III. Chap. XV.) with the production of salve-like substances.

Concentrated sulphuric acid in the hot carbonises the waxes. Dilute sulphuric acid is without any action on them.

Caustic alkalis hydrolyse the neutral esters more or less readily. Processes for the saponification of waxes will be considered in the following chapter, and in Vol. III. Chap. XV. under "Technology of Waxes."

ETHOLIDES

Bougault and Bourdier[3] describe a new class of vegetable waxes obtained from the leaves of coniferous plants (*Juniperus Sabina, J. communis, Picea excelsa, Pinus sylvestris, Thuja occidentalis*) by boiling out with 90 per cent alcohol. These waxes differ in their chemical constitution from all other waxes described in this work, in that they do not yield on saponification an alcoholic constituent like cetyl-, or melissylalcohol, both constituents of the waxes obtained by saponification having an acid character. Hence, if barium chloride solution be added to the alcoholic solution obtained on saponifying the waxes with alcoholic potash, and the dried precipitate be treated with petroleum ether or cold ether, nothing is thereby extracted. These waxes are therefore judged to be the esters of acids containing an alcoholic hydroxyl (alcoholiform) group, and the esters seem to have been produced by the radicle of the acidic constituent entering into chemical combination (esterification) with another molecule of the same or a similarly constituted alcoholiform acid. The authors therefore propose for these substances the name *etholides*, and compare them in their constitution with *Fischer's* peptides, which are formed from aminoacids. In the author's opinion it would appear more appropriate to compare these products with the polyricinoleic acids, which ricinoleic acid is capable of forming.

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[1] *Chem. Zeit.*, 1909, 1275.

[2] *Chem. Zeit.*, 1909, 779.

[3] *Compt. rend.*, 1908 (147), 1311.

The wax obtained from *Juniper Sabina* melts from 73° to 78° C., and can be resolved by treatment with solvents into fractions melting at 68°, 72°, 76°, and 82° C. respectively.

The acid value of the constituents into which the waxes are resolved by saponification varied from 25 to 54 ; the saponification value was about 230. As they are able to absorb acetyl groups in the acetylation test it is concluded by the authors that the constituents contain alcoholic hydroxyl groups. Hitherto two hydroxy acids have been isolated, viz. a hydroxylauric acid, $C_{12}H_{24}O_3$, melting at 84° C., which the authors term *sabinic* acid, and a hydroxypalmitic acid, $C_{16}H_{32}O_3$, termed *juniperic acid.*[1]

The wax obtained from *Thuja occidentalis* contains in addition to sabinic acid a small quantity of thapsic acid,[2] melting at 124° C. Thapsic acid is a dibasic acid $(CH_2)_{14}(COOH)_2$.

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[1] *Chem. Zeit.*, 1910 (150), 874.

[2] *Journ. Pharm. Chim.*, 1911 (7), 101.

CHAPTER II

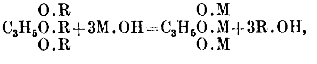
SAPONIFICATION OF FATS AND WAXES

THE chemical change which takes place on boiling fats with strong bases, and which results in the formation of glycerol and of salts of the higher fatty acids, has been termed " saponification." In a wider sense, however, every chemical process by which fats or waxes are resolved into their proximate constituents—glycerol and fatty acids in the case of fats, and higher alcohols and fatty acids in the case of waxes—is called saponification, even if no bases be employed to effect the reaction.

The term " saponification " is almost exclusively used in practice, its synonym " hydrolysis " being confined to papers of a scientific character. It would appear preferable to denote by the term " hydrolysis " all those reactions in which no strong bases are used, and to restrict the term " saponification " to those processes in which alcohols and soap are obtained as the ultimate products. But it is impossible to draw a sharp line of demarcation, as we have a number of processes in which practically complete resolution of the glycerides into their proximate constituents is brought about by an amount of bases which is far from sufficient to neutralise the fatty acids produced.

Saponification of Fats

The chemical change which fats undergo on being hydrolysed or saponified is expressed by the following equation :—



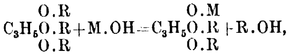
$$\text{(1)}\ C_3H_5\begin{array}{l}O.R\\O.R\\O.R\end{array}+3M.OH=C_3H_5\begin{array}{l}O.M\\O.M\\O.M\end{array}+3R.OH,$$

where R denotes the radicle of any fatty acid, and M stands for hydrogen (or a monovalent metal). (In the case of a bivalent metal equation (1) must be replaced by equation (4), p. 97.)

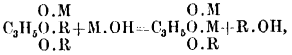
It follows from the equation that the products obtained by hydrolysis with water alone must exceed, theoretically, the quantity of fat or glycerides operated upon. This is clearly set out in the following table :—

Glyceride.	Formula.	Molecular weight.	Products obtained on saponification of 100 parts.		Excess over 100 parts.
			Fatty acids.	Glycerol.	
			Per cent.	Per cent.	Per cent.
Butyrin (Glycyl tributyrate)	$C_3H_5(O{\cdot}C_4H_7O)_3$	302	87·44	30·46	17·90
Caproin (Glycyl tricaproate)	$C_3H_5(O{\cdot}C_6H_{11}O)_3$	386	90·15	23·96	14·11
Caprylin (Glycyl tricaprylate)	$C_3H_5(O{\cdot}C_8H_{15}O)_3$	470	91·91	19·58	11·49
Caprin (Glycyl tricaprate)	$C_3H_5(O{\cdot}C_{10}H_{19}O)_3$	554	93·14	16·67	9·81
Laurin (Glycyl trilaurate)	$C_3H_5(O{\cdot}C_{12}H_{23}O)_3$	638	94·04	14·42	8·46
Myristin (Glycyl trimyristate)	$C_3H_5(O{\cdot}C_{14}H_{27}O)_3$	722	94·75	12·74	7·49
Palmitin (Glycyl tripalmitate)	$C_3H_5(O{\cdot}C_{16}H_{31}O)_3$	806	95·29	11·42	6·71
Stearin (Glycyl tristearate)	$C_3H_5(O{\cdot}C_{18}H_{35}O)_3$	890	95·73	10·34	6·07
Olein (Glycyl trioleate)	$C_3H_5(O{\cdot}C_{18}H_{33}O)_3$	884	95·70	10·41	6·11
Linolin (Glycyl trilinolate)	$C_3H_5(O{\cdot}C_{18}H_{31}O)_3$	878	95·67	10·48	6·15
Linolenin (Glycyl trilinolenate)	$C_3H_5(O{\cdot}C_{18}H_{29}O)_3$	872	95·63	10·55	6·18
Clupanodonin (Glycyl triclupanodonate)	$C_3H_5(O{\cdot}C_{18}H_{27}O)_3$	866	95·61	10·62	6·23
Ricinolein (Glycyl triricinoleate)	$C_3H_5(O{\cdot}C_{18}H_{33}O_2)_3$	932	95·93	9·87	5·80
Arachin (Glycyl triarachidate)	$C_3H_5(O{\cdot}C_{20}H_{39}O)_3$	974	96·09	9·45	5·54
Erucin (Glycyl trierucate)	$C_3H_5(O{\cdot}C_{22}H_{41}O)_3$	1052	96·39	8·74	5·13

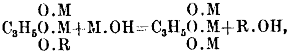
In the light of experiments made by *Geitel*[1] and by *Lewkowitsch*[2] equation (1) must be considered as summarising the following three equations :—

(1*a*) 

$$C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix}+M.OH=C_3H_5\begin{matrix}O.M\\O.R\\O.R\end{matrix}+R.OH,$$

(1*b*) 

$$C_3H_5\begin{matrix}O.M\\O.R\\O.R\end{matrix}+M.OH=C_3H_5\begin{matrix}O.M\\O.M\\O.R\end{matrix}+R.OH,$$

(1*c*) 

$$C_3H_5\begin{matrix}O.M\\O.M\\O.R\end{matrix}+M.OH=C_3H_5\begin{matrix}O.M\\O.M\\O.M\end{matrix}+R.OH,$$

These equations express the fact that hydrolysis (saponification) takes place in three stages, inasmuch as oils and fats pass from the triglyceride through the diglyceride and monoglyceride to the products of complete hydrolysis.

On carrying out " hydrolysis " or " saponification " on a practical scale, we cannot expect these three stages to take place consecutively, in distinct succession; or in other words, we cannot expect to find that the whole mass of triglycerides is at first hydrolysed exclusively to diglycerides (as is indicated by the equation (1*a*)), that the diglycerides are then broken down to monoglycerides (as is shown by the equation (1*b*)), and that finally the monoglycerides so formed are converted into glycerol and free fatty acid (1*c*). We shall rather find that the three phases, which are expressed by the above three equations, take place concurrently, so that at one and the same time a molecule of diglyceride may be broken down to monoglyceride and fatty acid, or a molecule of monoglyceride to glycerol and fatty acid, whilst a molecule of triglyceride is still intact, or is passing through the first phase. Therefore, on bringing about very rapid hydrolysis we shall not always be able to observe experimentally[1] the intermediate, transitory phases. If, however, hydrolysis or saponification be effected somewhat slowly, we may be able to find in the partially saponified mass: (1) unsaponified triglyceride, (2) diglyceride, (3) monoglyceride, (4) glycerol, and (5) free fatty acids.

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[1] *Journ. f. prakt. Chem.*, 1897 (55), 429.

[2] *Journ. Soc. Chem. Ind.*, 1898, 1107; *Proc. Chem. Soc.*, 1899, 190; *Berichte*, 1900, 89.

This has been verified to some extent by experiments of *Geitel*[2] and especially by those of *Lewkowitsch*.[3] I select from a large number of experiments I have made, the following as best demonstrating the fact that mono- and di-glycerides are formed as intermediate products in the course of saponification by means of caustic alkalis and caustic alkaline earths:—

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[1] Cp. in this respect Table 7, *Berichte*, 1900, 93; cp. also Lewkowitsch, *ibid.*, 1903, 3766; 1904, 881. Hence the opinion stated by Kellner (*Chem. Zeit.*, 1909, 453) on the strength of two experiments made by saponifying palm kernel oil with aqueous potash is entirely inconclusive. Cp. also B. Wegscheider, *Chem. Zeit.*, 1909, 1220.

[2] *Journ. f. prakt. Chem.*, 1897 (55), 429.

[3] *Journ. Soc. Chem. Ind.*, 1898, 1107; *Proc. Chem. Soc.*, 1899, 190; *Berichte*, 1900, 89.

[TABLE

Saponification of Tallow with Caustic Soda (Lewkowitsch)

Partially Saponified Tallow.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Insoluble Fatty Acids. Per cent.	Saponification Value.
Sample No. 1	12·2	17·1	94·4	207·9
,, ,, 2	12·8	24·3	94·7	210·2
,, ,, 3	20·9	18·9	94·9	206·6
,, ,, 4	31·4	9·7	95·8	203·1
,, ,, 5	45·4	15·3	96·0	208·15
,, ,, 6	77·9	11·2	97·0	206·7
,, ,, 7	105·8	52·03	...	237·65
,, ,, 8	126·8	65·6	...	252·5
,, ,, 9	145·3	78·9	...	269·0
,, ,, 10	152·4	61·8	...	252·7
Fatty Acids, obtained with Alcoholic Potash, Acetylated	...	8·8	99·5	212·8

Saponification of Tallow with Caustic Lime (Lewkowitsch)

Partially Saponified Tallow.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Insoluble Fatty Acids. Per cent.	Saponification Value.
Sample No. 1	20·6	13·9	93·3	210·05
,, ,, 2	40·9	22·3	93·5	215·3
,, ,, 3	79·0	16·6	93·5	214·6
,, ,, 4	46·1	15·7	94·5	212·3
,, ,, 5	50·98	27·9	93·87	221·4
,, ,, 6	59·6	28·0	93·6	223·75
,, ,, 7	114·2	...	94·97	216·5
,, ,, 8	122·05	27·2	95·5	226·7
,, ,, 9	110·9	42·0	93·8	239·35
,, ,, 10	128·4	...	95·57	218·7
Fatty Acids, obtained with Alcoholic Potash, Acetylated	...	6·7	99·5	212·8

[TABLE

Saponification of Cotton Seed Oil with Caustic Soda (Lewkowitsch)

Partially Saponified Oil.	Acid Value.	Acetylated Product.	
		Acetyl Value.	Saponification Value.
Sample No. 1 . . .	1·63	14·15	...
,, ,, 2 . . .	3·4	25·9	221·7
,, ,, 3 . . .	18·4	27·3	226·7
,, ,, 4 . . .	39·7	21·6	232·85
,, ,, 5 . . .	45·3	29·8	222·65
,, ,, 6 . . .	57·0	29·5	231·4
,, ,, 7 . . .	71·8	25·0	225·3
,, ,, 3 . . .	95·5	20·8	223·8
,, ,, 9 . . .	108·2	25·85	235·0
,, ,, 10 . . .	113·7	22·4	221·2
,, ,, 11 . . .	161·0	21·7	219·9
Original Oil, Acetylated . .	...	15·8	...
Fatty Acids, obtained with Alcoholic Potash, Acetylated	201·2	17·9	...

Saponification of Cotton Seed Oil with Caustic Lime (Lewkowitsch)

Partially Saponified Oil.	Acid Value.	Acetylated Product.		
		Acetyl Value.	Insoluble Fatty Acids. Per cent.	Saponification Value.
Sample No. 1 . . .	0·5	14·9	94·5	206·3
,, ,, 2 . . .	0·6	20·0	92·84	209·2
,, ,, 3 . . .	16·0	43·15	92·0	230·1
,, ,, 4 . . .	17·6	59·2	89·1	240·0
,, ,, 5 . . .	19·9	28·3	92·35	215·3
,, ,, 6 . . .	53·4	24·9	93·8	214·8
,, ,, 7 . .	73·2	32·4	93·6	223·4
Original Oil, Acetylated . .	0·0	11·7	93·5	...
Fatty Acids, obtained with Alcoholic Potash, Acetylated	199·45	13·8	99·4	216·4

Reasoning by analogy, hydrolysis by means of sulphuric acid should also take place in stages. Direct experimental proof may be found in the observation made by *Grün and Theimer*[1] that on hydrolysing distearo-α-chlorohydrin with 98 per cent sulphuric acid, there were obtained, besides still unchanged distearochlorohydrin, the following products: monostearochlorohydrin, monochlorohydrin, and stearic acid. These products of hydrolysis thus represent the three stages of diglyceride, monoglyceride, and free fatty acid.

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[1] *Berichte*, 1907, 1801.

Nevertheless *Grün and Corelli* arrived at the conclusion that by hydrolysing triglycerides with concentrated sulphuric acid diglycerides are formed to the exclusion of monoglycerides. Although *van Eldik Thieme* (see below) controverted this opinion by experimental evidence, *Grün and Corelli* repeated this statement recently.[1] This cannot, however, be accepted as correct. The supposed experimental evidence furnished by *Corelli* rests more or less on rule-of-three calculations, the basis for which is open to grave objection. More conclusive are the experiments of *van Eldik Thieme*,[2] who treated laurin with varying amounts of concentrated sulphuric acid at the temperatures stated in the following table, for thirty minutes, and then poured the product of the reaction on to pounded ice, so as to prevent hydrolysis. Then a sufficient amount of alcohol was added to yield a 60 per cent alcoholic solution, which was shaken out with a mixture of ether and petroleum ether. The solution was washed with water and the ether evaporated. The residue consisted in the case of experiment No. 3 of pure lauric acid; in experiments No. 1 and No. 2, besides lauric acid, notable amounts of non-hydrolysed glycerides were obtained. In the 4th experiment the non-hydrolysed glyceride amounted to 20 per cent, and appeared to contain dilaurin and monolaurin in addition to trilaurin.[3]

One Molecule of Trilaurin hydrolysed with Concentrated Sulphuric Acid

No.	Molecules of Sulphuric Acid of per cent:		Temperature.	Product contained Free Fatty Acid.
	100	94·6	°C.	Per cent.
1	6·5	...	18	86·6
2	26·0	...	1-2	95·5
3	52·0	...	1-2	100·0
4	...	52·0	1-2	80·0

In a more recent paper the same author[4] shows (as would seem to follow from the experimental evidence under No. 3 of the foregoing table) that an addition-product of laurin and concentrated sulphuric acid is formed which is only stable at a low temperature and is readily hydrolysed by water, especially at a higher temperature. *Van Eldik Thieme* was able to show that monolaurin and dilaurin are formed as intermediate products, if the hydrolysis is carried to practical com pletion. The resolution of trilaurin by concentrated sulphuric acid may be expressed by the following set of equations (*van Eldik Thieme*):—

---

[1] *Zeits. f. angew. Chem.*, 1912, 665.

[2] *Proceed. K. Akad. van Wetensch.*, Amsterdam, 1908, 855; cp. also Grün and Theimer, *Berichte*, 1907, 1801.

[3] Cp. also Vol. II. Chap. XIV. "Butter Fat."

[4] *Zeits. f. prakt. Chem.*, 1912 (85), 300.

$$\text{(1)}\ \mathrm{CH_2.OR-CH.OR-CH_2.OR+nH_2SO_4=CH_2.O.SO_3H-CH.OR-CH_2.OR}$$

or:—

$$\mathrm{CH_2.OR-CH.O.SO_3H-CH_2.OR+(ROH.H_2SO_4)},$$

$$\text{(2)}\ \mathrm{CH_2.OR-CH.OR-CH_2.OR+mH_2SO_4 =CH_2.O.SO_3H-CH.O.SO_3H-CH_2.OR}$$

or:—

$$\mathrm{CH_2.O.SO_3H-CH.OR-CH_2.O.SO_3H+(2ROH.H_2SO_4)},$$

$$\text{(3)}\ \mathrm{CH_2.OR-CH.OR-CH_2.OR+rH_2SO_4 =CH_2.O.SO_3H-CH.O.SO_3H-CH_2.O.SO_3H+(3ROH.H_2SO_4)},$$

or, what is more likely, by the following set:—

$$\text{(1}a\text{)}\ \mathrm{CH_2.O.SO_3H-CH.OR-CH_2.OR+sH_2SO_4 =CH_2.O.SO_3H-CH.OR-CH_2.O.SO_3H+(ROH.H_2SO_4)},$$

or:—

$$\mathrm{CH_2.OR-CH.O.SO_3H-CH_2.OR+sH_2SO_4 =CH_2.O.SO_3H-CH.O.SO_3H-CH_2.OR+(ROH.H_2SO_4)},$$

$$\text{(2}a\text{)}\ \mathrm{CH_2.O.SO_3H-CH.OR-CH_2.O.SO_3H+pH_2SO_4 =CH_2.O.SO_3H-CH.O.SO_3H-CH_2.O.SO_3H+(ROH.H_2SO_4)},$$

or:—

$$\mathrm{CH_2.O.SO_3H-CH.O.SO_3H-CH_2.OR+pH_2SO_4 =CH_2.O.SO_3H-CH.O.SO_3H-CH_2O.SO_3H+(ROH.H_2SO_4)}.$$

Similarly, glyceryl trinitrate is hydrolysed by a 70 per cent sulphuric acid to glyceryl dinitrate, and glyceryl dinitrate in its turn to mononitrate and glycerol.[1] In the case of glyceroltrisulphuric acid the correctness of the theory can be demonstrated even more conveniently inasmuch as the glycerolmonosulphuric acid formed as an intermediate product is somewhat resistant to the action of water and requires to be boiled with water for some prolonged time before it is finally dissociated to glycerol and sulphuric acid.[2]

The author's views have been repeatedly attacked, and for a short time the objections raised against them appeared to be supported by considerations based on some physico-chemical measurements. Whilst purely chemical objections have been shown by the author himself to be irrelevant, more recently published investigations (by a number of observers) of a physico-chemical nature have proved undoubtedly that hydrolysis does take place in stages. For the voluminous literature, to some extent of a controversial nature, the reader must be referred to the sources given in the footnote.[3]

Kellner[4] complemented the author's chemical experiments by determining the percentage of glycerol, which partially hydrolysed glycerides yield. In the case of hydrolysis in an autoclave by means of bases, then by hydrolysis with the aid of the Twitchell reagent and the castor seed ferment, the estimation of glycerol in the partially hydrolysed fats proved that lower glycerides (mono- and di-glycerides) were present. The contrary conclusion arrived at by *Kellner* in the case of saponification with caustic potash has been shown by the author to be inconclusive (see p. 76). Finally, *V. Fortini*,[1] employing the chemical method proposed by the author, fully confirmed the latter's earlier results and conclusions by determining the acetyl values of partially saponified triglycerides, alcoholic potash being the saponifying agent.

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[1] Will., *Berichte*, 1908, 1107.

[2] van Eldik Thieme, *Journ. f. prakt. Chem.*, 1912 (85), 306.

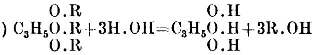
[3] *Jahrbuch d. Chem.*, 1897, vii. 367 (Geitel); 1898, viii. 390 (Lewkowitsch); 1899, ix. 352 (Lewkowitsch); 1902, xii. 362 (Balbiano); 1904, xiv. 429 (Balbiano; Fanto); 1905, xv. 419 (Kremann; Fanto); 1906, xvi. 396 (Kremann; Marcusson; Lewkowitsch); 1907, xvii. 406 (J. Meyer; Kremann; Wegscheider; Fanto and Stritar); *Journ. f. prakt. Chem.*, 1908, 364 (Kremann); *Jahrbuch d. Chem.*, 1908, xviii. 405 (Lewkowitsch); 1909, xix. (Kellner); J. Meyer, *Zeits. f. phys. Chem.* 66, 81.

[4] *Chem. Zeit.*, 1909, 453, 662.

In full agreement with the experiments is the evidence afforded by the synthesis of triglycerides, as it is possible to build them up from glycerol and fatty acid to monoglyceride, from the monoglyceride to diglyceride, and from the diglyceride to triglyceride (see Chap. I.).

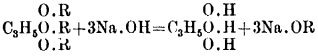
The occurrence of dierucin (in old rape oil), for a long time looked upon as an exceptional phenomenon, is now satisfactorily explained, and the presence of mono- and di-glycerides in rancid fats becomes very probable. This is well illustrated by the changes olive oil undergoes in stored olives (see Vol. II. Chap. XIV. " Olive Oil ").

Since in the absence of water no hydrolysis can take place, water must be considered as the hydrolysing agent, whether it be employed alone, or whether its action be assisted by catalytic agents, such as acids or ferments. In these cases the reaction is expressed by the following equation :—

(2) 

$$C_3H_5\begin{array}{l}O.R\\O.R\\O.R\end{array}+3H.OH=C_3H_5\begin{array}{l}O.H\\O.H\\O.H\end{array}+3R.OH$$

If bases be chosen as catalysts (catalysers), a subsequent chemical reaction takes place, viz. the combination of the base with the fatty acids. Thus, if in equation (1) M be a monovalent metal, *e.g.* sodium, the final products will be glycerol and soda soap, as expressed by the equation :—

(3) 

$$C_3H_5\begin{array}{l}O.R\\O.R\\O.R\end{array}+3Na.OH=C_3H_5\begin{array}{l}O.H\\O.H\\O.H\end{array}+3Na.OR$$

On a large scale fats are hydrolysed by various methods. These will be considered from a technical point of view in Vol. III. Chap. XV. Here the underlying principles will be discussed in a short review of the several processes leading to hydrolysis.

It has been pointed out already (p. 48) that at a high temperature water alone can effect hydrolysis.[2] This reaction can be realised in practice, and has indeed been carried out on a large scale by heating fats with water under a pressure of 15 atmospheres (which is equivalent to a temperature of 202° C.), or by distilling fats in a current of superheated steam, when fatty acids, together with the glycerol formed, are carried over by the steam.

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[1] *Chem. Zeit.*, 1912, 117. For a criticism of this paper cp. *ibid.*, 1913, 541 (J. Meyer).

[2] It has been shown above (bog butter, etc.) that, given sufficient length of time, water at the ordinary temperature can effect complete hydrolysis.

The following table, due to *Klimont*,[1] is instructive as showing the progress of hydrolysis at pressures of 7 and 15 atmospheres respectively :—

Aqueous Saponification of Neutral Fats under Pressure

30 grms. of Oil or Fat and 500 grms. of Water.

Kind of Fat or Oil.	At a Pressure of 7 Atmospheres. Acid Values after				At a Pressure of 15 Atmospheres. Acid Values after			
	2 hrs.	4 hrs.	6 hrs.	8 hrs.	1½ hrs.	2 hrs.	4 hrs.	6 hrs.
Cocoa nut oil . .	0·1	0·3	0·5	0·9	78·6	90·2	123·9	185·5
Japan wax . .	4·8	5·3	9·4	13·1	...	12·3	32·5	46·1
Tallow . . .	17·5	37·3	67·3	84·8	...	62·3	106·3	155·8
Tallow stearine .	15·3	38·3	65·5	81·6	...	60·4	98·7	160·3
Cacao butter . .	12·3	24·5	45·1	62·6	...	34·5	76·1	160·5
Olive oil . . .	15·1	32·1	53·0	71·4	...	66·5	114·5	159·5
Sesamé oil . .	14·3	31·1	56·2	76·0	...	61·7	108·4	153·7
Cotton seed oil. .	10·0	23·2	36·3	51·7	...	42·2	80·2	128·6
Linseed oil . .	11·4	21·1	43·3	56·1	...	38·1	78·5	130·5

On halving the acid values we obtain approximately the extent of hydrolysis expressed in percentages ; in the case of cocoa nut oil, however, the figures should be multiplied by 0·4.

The temperature at which hydrolysis took place is fixed approximately by the pressure given, viz. about 170° C. at 7 atmospheres and 200° C. at 15 atmospheres.

The data contained in the following table show the influence of the higher pressure (and inferentially of the higher temperature) in the case of a laboratory experiment with olive oil.

Acid Values after 6 *hours' Treatment with Steam*

Pressure, Atmospheres .	3	5	6	7	10	13	15
Approx. Temperature, ° C.	144	159	165	170	184	195	202
Acid value	6·4	35·5	41·7	53·0	62·3	108·3	159·5

Experiments made with superheated steam at a pressure of about 3 atmospheres, but at varying temperatures, are detailed in the following table :—

---

[1] *Zeits. f. angew. Chem.*, 1901, 1270.

[TABLE

Acid Values after 1½ hour's treatment at the following temperatures

Kind of Oil.	Original Acid Value.	170° C.	180° C.	190° C.	200° C.
Cocoa nut oil . .	0	. .	. .	0·2	0·4
Olive oil . . .	0	0·6	1·0	3	8·9
Sesamé oil . .	0	0·6	0·9	2·5	7·4

It has also been pointed out that hydrolysis can be accelerated and the temperature reduced if the action of water be assisted by the presence of a catalytic agent. A suitable catalyst is hydrochloric acid, which obviously does not take part in the chemical change, but merely accelerates the hydrolysis primarily brought about by water. This is illustrated by a series of experiments made by *Lewkowitsch*,[1] and detailed in the following table :—

Hydrolysis of Oils and Fats by means of Hydrochloric Acid, Sp. Gr. 1·16
(Lewkowitsch)

100 grms. of Oil or Fat boiled with 100 c.c. of Acid.

Oil or Fat.	Original Acid Value.	Acid Value after 24 Hours' Boiling.	Acid Value of completely Hydrolysed Oil or Fat.
Cotton seed	0·35	143·9	202
Whale	6·01	157·3	195
Rape	2·16	131·7	185
Lard	1·25	140·3	201
Tallow	11·15	150·0	200
Cocoa nut . . .	18·75	204·9	260
Castor	1·22	49·14	190

In these experiments a certain amount of hydrochloric acid had escaped as gas ; hence, in the experiments described in the following table, a fresh amount of acid was used after each sample had been taken from the bulk :—

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[1] *Journ. Soc. Chem. Ind.*, 1903, 67.

[TABLE

Hydrolysis of Oils and Fats by means of Hydrochloric Acid, Sp. Gr. 1·16 (*Lewkowitsch*)

100 grms. of Oil or Fat and 100 c.c. of Acid ; fresh acid used after each sample had been taken.

Oil or Fat.	Original Acid Value.	Acid Values after										Acid Value of completely hydrolysed Oil or Fat.
		2 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.	
Cotton seed .	0·35	18·42	79·6	95·51	116·2	136·4	144·9	155·7	164·8	168·2	175·8	202
Whale . .	6·01	26·69	101·3	120·3	142·7	155·4	162·3	170·0	172·0	...	...	195
Rape . .	2·16	19·66	75·06	89·57	107·2	120·1	127·3	134·2	140·3	144·0	151·8	185
Lard . .	1·25	14·51	84·78	116·8	139·8	149·4	152·1	162·7	168·0	173·0	177·0	201
Tallow . .	11·15	43·39	112·5	131·7	153·2	167·0	173·3	178·9	183·3	185·2	186·8	200
Cocoa nut .	18·75	79·73	184·2	210·5	221·4	230·8	233·4	239·8	241·1	246·1	250·1	260
Castor . .	1·22	44·4	47·3	49·0	51·4	51·4	47·9	49·2	46·8	44·4	41·64	190

The exceptional behaviour which castor oil exhibits can only be explained by the different constitution of its fatty acids, and the ready formation of polymerisation products (cp. Chap. I. p. 45, Chap. XV.).

The following three tables describe a number of experiments which

Hydrolysis of Oils and Fats by means of Hydrochloric Acid, Sp. Gr. 1·16 (*Lewkowitsch*)

100 grms. of Oil or Fat, containing Free Fatty Acids, and 100 c.c. of Acid ; fresh acid used after each sample had been taken.

Oil.	Original Acid Value.	Acid Values after										
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Cotton seed . .	10·51	37·69	71·1	88·73	94·85	103·9	113·6	117·1	119·7	125·6	132·1	140·3
Whale . . .	15·16	41·44	85·84	105·0	123·2	147·3	158·6	164·3	173·9	175·3	...	...
Rape . . .	9·17	32·1	61·31	75·36	78·09	92·55	101·4	110·1	128·9	132·6	139·6	145·2
Lard . . .	11·3	14·52	49·58	71·46	86·36	101·2	116·8	128·5	138·0	147·3	148·7	155·0
Tallow . . .	20·14	49·41	114·9	140·7	154·5	167·6	175·8	178·6	182·9	183·3	189·0	189·4
Castor . . .	10·98	46·8	50·9	46·8	47·4	47·9	48·5	48·4	46·8	43·3	47·11	48·34

Lard boiled with Hydrochloric Acid and 1 *per cent of the following Substances* (*Lewkowitsch*)

	Original Acid Value.	Acid Values after										
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Mercury . . .	1·25	12·32	35·24	63·34	96·44	133·5	145·5	154·0	164·4	169·1	174·0	174·6
Copper sulphate .	1·25	19·68	53·06	82·45	89·81	131·8	146·7	153·1	156·9	164·6	171·3	175·4
Mercuric oxide .	1·25	29·47	66·74	88·48	129·1	149·3	156·0	160·2	167·4	178·0	178·1	182·9
Zinc . . .	1·25	17·88	85·94	127·3	146·0	163·7	168·0	172·7	178·5	182·0	183·1	185·7
Zinc-dust . .	1·25	17·07	58·83	88·23	98·13	118·1	129·7	136·7	144·0	150·8	156·0	163·0
Aluminium chloride	1·25	16·88	46·91	78·65	100·7	125·4	136·8	138·9	152·7	159·4	166·7	166·8
Nitrobenzene . .	1·25	56·77	103·5	120·6	129·3	147·1	152·3	158·9	163·2	166·9	168·7	171·1
Aniline . . .	1·25	18·16	49·56	86·3	96·44	119·4	131·1	134·8	135·6	142·1	150·4	152·1

Lard containing Free Fatty Acids boiled with Hydrochloric Acid and 1 *per cent of the following Substances* (*Lewkowitsch*)

	Original Acid Value.	Acid Values after										
		2 hrs.	4 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.
Mercury . . .	11·3	21·64	48·82	80·0	102·2	119·4	134·0	144·0	151·3	156·4	160·4	161·6
Copper sulphate .	11·3	56·91	99·97	115·0	142·0	159·9	169·0	175·6	178·7	181·1	183·4	186·2
Mercuric oxide .	11·3	32·24	67·47	99·9	108·5	113·8	144·8	150·3	153·0	154·5	157·4	161·2
Zinc . . .	11·3	42·04	74·65	86·39	117·6	134·8	146·8	155·6	158·3	165·8	169·4	174·6
Zinc-dust . .	11·3	16·96	33·0	56·05	72·6	88·49	100·0	106·4	109·6	118·1	123·9	134·2
Aluminium chloride	11·3	62·15	90·56	121·0	127·3	138·5	145·3	145·6	151·4	156·2	159·2	161·9
Nitrobenzene . .	11·3	32·45	76·74	111·0	122·3	129·9	134·0	139·0	143·6	150·0	156·3	161·9
Aniline . . .	11·3	34·51	74·1	74·76	93·26	106·9	119·3	124·7	128·9	133·9	138·2	141·0

were carried out with a view to accelerating still further, if possible, the hydrolysis brought about by the aid of hydrochloric acid.[1]

The numbers given in the tables show that hydrolysis becomes very much slower when about 75 per cent of the neutral fats has been hydrolysed. The fact that under the conditions of the experiments it was very difficult to keep up a thorough intermixture of fat and acidulated water, satisfactorily explains this slowing down of the reaction. It may be safely assumed that provided a thorough intermixture, as in an emulsion, could be brought about, hydrolysis would proceed much more rapidly (see below), for the catalytic action of hydrochloric acid is even exercised at the ordinary temperature, in course of time, as is proved by the following experiment carried out in my laboratory : [2]—

100 grms. of cotton seed oil shaken through with 50 c.c. of hydrochloric acid :

Original acid value		0·35
Acid value after	1 day	1·22
,, ,,	7 days	3·66
,, ,,	107 ,,	95·10
,, ,,	213 ,,	130·20

Much better results are obtained by employing as a catalyst *concentrated sulphuric acid*, which seems to act to some extent as an emulsifying agent in the technical process of *hydrolysis by means of concentrated sulphuric acid* (Vol. III. Chap. XV. " Acid Saponification," " Sulphuric Acid Saponification "). In the case of saturated glycerides the sulphuric acid acts solely as a catalyst. In the case of olein a similar action may be assumed to take place at first so that the action of sulphuric acid could consist, in the first instance, in the formation of sulpho-compounds of glycerides (p. 62), the composition of which has been investigated by *Geitel*.[3] At higher temperatures, such as are employed in practice, these are decomposed rapidly to compounds forming a complete emulsion with water and fats, so that on agitating the emulsion with steam, complete hydrolysis to glycerol and fatty acids is gradually brought about. As the ordinary oils and fats may be looked upon as consisting chiefly of mixed glycerides, the action of the acid consists both in behaving as a catalyst and as a chemical agent, producing in this latter case well-defined chemical compounds.

The earliest experiments on the " acid saponification " process are to be found in *Dictionnaire de Maquer*, t. iii. 370, and are ascribed to *Cornette*, 1777. In 1790, *Papillon* recommended the use of a fat and sulphuric acid as a process employed in England commercially. Therefore *Chevreul* speaks of the sulphuric acid saponification as a well-known process. But there is no mention made yet of technical application.

Experiments instituted in my laboratory,[2] and detailed in the following table, illustrate the progress of hydrolysis :—

---

[1] Berthelot (*Chim. organ.* ii. 82) states that olein after treatment with aqueous hydrochloric acid for 96 hours at 100° C was hydrolysed to some extent, but not completely.

[2] Unpublished results.

[3] *Journ. f. prakt. Chem.*, 1888 (37), 53. Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1897, 392.

Tallow hydrolysed with 4 per cent of concentrated Sulphuric Acid at 120° *C.* (*Lewkowitsch*)

	Product contained Free Fatty Acids. Per cent.
Sample taken after 1 hour's steaming . .	42·1
,, ,, 2 hours' ,, . .	65·1
,, ,, 3 ,, ,, . .	79·3
,, ,, 4 ,, ,, . .	83·7
,, ,, 5 ,, ,, . .	88·6
,, ,, 6 ,, ,, . .	91·7
,, ,, 7 ,, ,, . .	91·7
,, ,, 8 ,, ,, . .	92·3
,, ,, 9 ,, ,, . .	93·0

It should, however, be pointed out that the fatty acids thus obtained are not exclusively the hydrates of the acid radicles contained originally in the glycerides, as sulpho-fatty acids are formed first, which, in the case of the unsaturated fatty acids, lead to the formation of hydroxylated fatty acids (cp. Chap. III., and Vol. III. Chap. XV. " Conversion of Oleic Acid into Candle Material ").

In the following table I collate a number of experiments (unpublished) carried out by me with a view to ascertaining the amount of hydrolysis brought about by sulphuric acid of varying strength. It will be seen that there is a gradual decrease of hydrolysis with the decrease in the strength of the acid until, when using acid containing only 60 per cent of SO_4H_2, the hydrolysing action ceases altogether. With regard to the action of dilute sulphuric acid, it has been shown above (p. 63) that oils and fats, *i.e.* triglycerides, are practically not acted upon by diluted sulphuric acids. Inasmuch as the completion of the hydrolysis in the sulphuric acid saponification process is effected by steaming, *e.g.* in dilute solution, it would follow that the lower glycerides (*i.e.* mono- and di-glycerides) which (according to theory) are formed, would be more readily attacked by dilute acid. This

Hydrolysis of Tallow, containing 6·2 *per cent Free Fatty Acids, with* 4 *per cent of Sulphuric Acid of varying strength*
(*Lewkowitsch*)

Sulphuric Acid containing per cent SO_4H_2:	Per cent Fatty Acids. After steaming for hours:																					
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22
98	42·1	65·1	79·3	83·7	88·6	91·7	91·7	92·3	93·0	92·3	93·0	93·6	93·6	93·0	93·6	93·6						
90	37·2	47·7	57·6	65·1	72·5	76·0	80·0	81·8	83·6	86·2	88·0	86·8	88·6	88·6	89·0	90·5	90·5					
85	34·1	45·2	50·8	62·6	68·2	73·1	75·0	76·2	79·4	84·3	84·9	89·3	89·3	89·3	89·9	89·9	89·9					
80	31·6	45·2	57·6	65·1	73·1	75·4	79·3	80·6	83·7	85·5	87·4	83·6	89·0	89·9	89·9	89·9						
70	15·5	16·7	17·9	18·3	18·6	20·3	24·8	26·5	28·5	31·0	32·6	34·7	35·4	37·0	39·0	40·1	42·7	45·2	46·5	47·7	47·7	47·7
60	6·2	6·2	6·2	6·2																		
50	6·2	6·2	6·2	6·2	6·8																	

theoretical postulate is clearly brought out by the experiments of *van Eldik Thieme*, detailed in the following table :—

5 grs. of Tri-, Di-, and Mono-laurin boiled 5 minutes with Sulphuric Acid of the Concentrations given below.

Acid Values.	100 c.c. containing 0·97 gr. H_2SO_4.	100 c.c. containing 3·83 gr. H_2SO_4.	100 c.c. containing 10·83 gr. H_2SO_4.
Trilaurin . .	0·25	0·24	0·83
Dilaurin . .	0·82	1·19	2·10
Monolaurin . .	15·21	53·51	104·61

A similar but much more pronounced emulsifying action than is obtained with concentrated sulphuric acid is produced by means of the sulpho-aromatic compound introduced by *Twitchell*.[1] By adding about 1 to 2·5 per cent of this reagent to oils and fats, and heating them for a certain length of time in a current of steam, they are almost completely hydrolysed, especially if a few per cent of free fatty acids be present, as these seem to be necessary to induce the reaction or at least influence favourably the starting of the hydrolysis. A series of experiments carried out in my laboratory gave the results set out in the following table[2] :—

---

[1] English patent 4741, 1898 ; United States patent 601,603 ; German patent 114,491. *Journ. Amer. Chem. Soc.*, 1900, 22. Cp. also Vol. III. Chap. XV., and "Turkey Red Oils," Vol. III. Chap. XV.

[2] Hitherto unpublished results.

[TABLE

Hydrolysis of Oils and Fats by means of Twitchell's Reagent (*Lewkowitsch*)

100 grms. of Oil or **Fat**, steamed up in open flasks with 1 per cent of the Sulpho-aromatic Compound.

Oil or Fat.	Original Acid Value.	Acid Value after															
		2 hrs.	7 hrs.	9 hrs.	12 hrs.	14 hrs.	16 hrs.	18 hrs.	20 hrs.	22 hrs.	24 hrs.	26 hrs.	28 hrs.	30 hrs.	32 hrs.	34 hrs.	36 hrs.
Cotton seed .	5·67	8·75	61·28	99·8	129·4	137·6	148·7	150·1	155·9	157·9	161·4	164·5	165·2	166·3	167·0	168·4	168·9
Whale . .	6·01	14·99	48·69	63·72	72·42	80·8	84·31	85·82	89·68	90·71	91·67	91·67	91·7	94·69	97·88	98·07	98·9
Rape . .	2·16	8·4	23·24	30·59	44·26	50·57	53·6	55·4	56·58	56·72	57·91	59·58	60·6	61·46	61·61	61·87	62·3
Lard . .	2·6	11·37	38·66	58·73	82·42	90·81	98·49	107·3	107·9	109·0	110·5	112·0	115·2	118·3	118·6	119·1	120·2
Tallow . .	11·15	15·03	25·68	43·44	49·39	50·11	52·03	53·1	53·85	55·6	57·11	59·82	60·23	63·95	66·2	67·3	68·5
Cocoa nut .	18·75	114·0	221·4	232·9	233·2	236·0	236·2	237·2	237·9	238·9	239·5	239·8	239·8	240·6	240·9	241·0	241·2

I have further instituted a series of experiments with "sulpho-aromatic compounds" prepared from naphthalene, anthracene, and phenanthrene respectively. From the numbers given in the following two tables it will be seen that the reagent prepared from naphthalene is much more effective than that obtained from anthracene or phenanthrene, but in each case hydrolysis practically reaches 100 per cent after a given time.

Hydrolysis of Cotton Seed Oil by means of 1 *per cent of Sulphostearo-aromatic Compounds* (*Lewkowitsch*)

(*a*) Neutral Oil

Sulphostearo-aromatic Compound of	Original Acid Value.	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	39 hrs.	45½ hrs.
Naphthalene .	1·22	146·7	190·7	201·4	211·4	...	...	...
Anthracene . .	1·22	2·5	21·8	76·3	170·7	186·5	190·7	...
Phenanthrene .	1·22	45·7	125·7	177·7	183·6	194·1	201·2	...

(*b*) Oil containing Free Fatty Acids

Sulphostearo-aromatic Compound of	Original Acid Value.	6½ hrs.	13 hrs.	19½ hrs.	26 hrs.	32½ hrs.	39 hrs.	45½ hrs.
Naphthalene .	8·3	30·9	194·1	216·9	216·7	...	...	...
Anthracene . .	8·3	15·01	60·5	112·4	147·2	148·2	189·8	202·8
Phenanthrene .	8·3	42·3	159·9	156·4	181·6	184·2	204·2	204·2

The composition of the reagent is stated by *Twitchell*[1] to be $C_6H_4(SO_3H)C_{18}H_{35}O_2$ in the case of benzene being used for its preparation, $C_{10}H_6(SO_3H)C_{18}H_{35}O_2$ in the case of naphthalene, and $C_6H_3(OH)(SO_3H)C_{18}H_{35}O_2$ in the case of phenol.

The preparation of a "*Twitchell* reagent" from sulphonated higher alcohols, such as occur in (wool wax) wool grease, beeswax, and other waxes (cetyl alcohol) or from the waxes themselves, has been claimed in a Patent Application on the part of the *Vereinigte Chemische Werke*, but the application has been withdrawn. Later the *Vereinigte Chemische Werke* patented the preparation of a *Twitchell* reagent[2] from aromatic sulphonated fatty acids or oils and fats (such as castor oil), which had been previously subjected to a hydrogenating process (see Vol. III. "Hydrogenised Fats"); in other words, the "*Twitchell* reagent," instead of being prepared from oleic acid, is obtained from a sulphonated, practically saturated hydroxylated fatty acid.

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[1] *Journ. Amer. Chem. Soc.*, 1900, 22.

[2] English patent 749, 1912; French patent 439,209; United States patent 1,058,633; and German patent application of 2nd February 1912.

Petroff[1] proposes a hydrolysing agent, prepared on the lines of the *Twitchell* reagent, from petroleum hydrocarbons by treatment with concentrated sulphuric acid.

It should be pointed out that the fatty acids obtained by this process have not undergone any change, and that they therefore represent the hydrates of the fatty acid radicles which are originally contained in the oils and fats employed. This should be emphasised, inasmuch as it shows that whereas in the course of hydrolysis by means of concentrated sulphuric acid secondary reactions occur, such secondary reactions do not take place in the *Twitchell* method of hydrolysis. Herein may be found proof for the view that no true sulphonated acids are formed. (For the technical application of this process see Vol. III. Chap. XV. " Saponification by means of *Twitchell's* Reagent.")

It would thus appear that the action of the *Twitchell* reagent, which must naturally be looked upon as a chemically acting substance, is a purely catalytic one, and may be put in a line with the action of ferments[2] which accelerate hydrolysis without apparently undergoing any chemical change. Such phenomena as these seem to show the extremely important influence which complete emulsion with water has on the progress of hydrolysis (cp. Vol. III. Chap. XV. " Candle Manufacture," " Soap Manufacture "). With regard to the hydrolysing properties of phenolsulphonic acid see below, p. 100.

On washing the *Twitchell* reagent with brine until no more acid passes into solution, a product is obtained which still possesses all the emulsifying powers of the " *Twitchell* reagent," but no longer effects hydrolysis. The hydrolysing action is restored on adding a small amount of a stronger acid. *Grimlund*[3] is of the opinion that the " *Twitchell* reagent " consists of two different substances: (1) a body of unknown composition soluble in brine; (2) the hydrolysing constituent which consists of sulphuric acid and aromatic sulpho-acids.

The foregoing observations confirm the necessity of working in an acid solution.

It has been pointed out above (p. 42) that free fatty acids, presumably due to slight hydrolysis of glycerides, occur in seeds. *Pelouze*[4] showed first in 1855 that oil seeds (linseed, poppy seed, cameline seed, rape seed, mustard seed, arachis kernels, sweet and bitter almonds) contain a substance which is capable of producing comparatively rapid hydrolysis of the oils contained in the seeds, and *Müntz* in 1871 demonstrated that the first phase of the utilisation of the fatty matter (in seeds) runs concurrently with hydrolysis of the oils and fats, and that the acidity is due to free fatty acids liberated from the neutral glycerides. These observations were confirmed in 1876 by *Schützenberger*. *Maillot*[5] in 1880 endeavoured to isolate from castor seed a soluble ferment which was expected to possess lipolytic properties. Experiments by *J. R. Green*[1] and *W. Siegmund*[2] firmly established the fact that the seeds have lipolytic action. Comparatively little attention, however, was paid to this subject from a technical point of view until *Connstein, Hoyer, and Wartenberg*,[3] by an extended series of experiments, showed that the ferment contained in castor seed is capable of accelerating considerably the hydrolysis of triglycerides, provided they be completely emulsified with slightly acidulated water. From their observations I collate the numbers contained in the following table :—

---

[1] French patent 437,336; English patent 27,244, 1912.

[2] Cp. Lewkowitsch, *Jahrbuch der Chemie*, 1907, xvii. 407.

[3] E. Grimlund, *Zeits. f. angew. Chem.*, 1912, 1326; *Bull. Soc. Chim. de France*, 1909, *Conférence XV.*

[4] *Compt. rend.*, 1855, 605; *Ann. de Chim. et de Phys.*, 1855 (45), 319.

[5] *Etude comparée du pignon et du ricin de l'Inde*, Nancy, 1880.

Hydrolysis of Oils and Fats by means of Castor Seed Ferment

Oil or Fat	Grms.	Castor Seed.		Fatty Acids formed. Per cent.	After Hours:	Temperature.	Acid.
		Original.	Extracted.				
		Grms.	Grms.			°C.	Grms. $^n/_{10}SO_4H_2$
Tallow . . .	6·5	5	...	72	19	35	4 ,, ,,
Bone fat . .	6·5	5	...	81	19	35	4 ,, ,,
Cotton seed oil .	6·5	5	...	84	19	35	4 ,, ,,
Palm oil . .	6·5	5	...	87	19	35	4 ,, ,,
Rape oil . .	6·5	5	...	84	19	35	4 ,, ,,
Palm nut oil .	16·5	5	...	76·6	20	Ordinary	8 ,, ,,
Arachis oil . .	25	...	1·3	100[5]	96	,,	5 ,, ,,
Rape oil . .	25	...	1·3	100[5]	96	,,	5 ,, ,,
Poppy seed oil .	25	...	1·3	100[5]	96	,,	5 ,, ,,
Linseed oil . .	50	...	5	83	24	,,	10 ,, ,,
Blubber oil (I.) .	50	...	5	76	24	,,	10 ,, ,,
,, ,, (II.) .	50	...	5	84	24	,,	10 ,, ,,
Olive oil . .	50	...	5	86	24	,,	10 ,, ,,
Sesamé oil . .	50	...	5	85	24	,,	10 ,, ,,
Almond oil . .	50	...	5	90	24	,,	10 ,, ,,
Cacao butter . .	50	...	5	92	24	,,	10 ,, ,,
Palm oil[4] . .	75	...	7·5	77	6	,,	15 ,, ,,
,, ,, . .	75	...	7·5	96	22	,,	15 ,, ,,
Cotton seed oil .	75	...	1·5	82	44	,,	15 ,, ,,
,, ,, .	100	...	5	87	44	,,	10 ,, ,,
,, ,, .	75	...	7·5	79	24	,,	15 ,, ,,
Triolein . .	10	...	...	50·6	24	...	...
Triacetin . .	10	...	0·5	0·4	24	...	2 ,, ,,
Tributyrin . .	10	...	...	9·5	24	...	...

The last two experiments would seem to show that whereas the glycerides of the higher fatty acids are comparatively easily hydrolysed, glycerides of the lower fatty acids offer much greater resistance. *Urbain, Saugon, and Feige*[1] have, however, demonstrated that free fatty acids somewhat inhibit the action of the ferment; and that this inhibiting action increases, the lower the molecular weight of the free fatty acid. These observers conjecture that in the case of triacetin and tributyrin the free acetic and butyric acids stopped the progress of hydrolysis; this was confirmed by *Hoyer*;[2] on the other hand, *A. E. Taylor*[3] stated that triacetin is very readily hydrolysed in the presence of castor seed ferment.

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[1] *Proc. Roy. Soc.*, 1890, 370 ; cp. also Green and Jackson, *ibid.*, 1905, 69. *Nature*, 1909 (82), 100. In Green's opinion, the view that enzymes initiate and maintain the process of germination appears to be erroneous. This does not, of course, affect the view of the present author that the enzymes act as catalysts, which only do their work if favourable conditions present themselves.

[2] *Monatsh. f. Chem.*, 1890, 272.

[3] *Berichte*, 1902, 3989.

[4] The percentages of free fatty acids in the original palm oils were not stated.

[5] These numbers are undoubtedly too high, and must be due to experimental errors, as the castor seed ferment is also capable of inducing the reverse reaction, viz. formation of glycerides from fatty acid and glycerol, so that complete hydrolysis is theoretically impossible ; cp. A. E. Taylor, *Journ. of Biolog. Chem.*, 1906, ii. 87. Moreover, *Nicloux* has shown that the products of the hydrolysis have an inhibiting effect.

The extent of hydrolysis stands in a definite proportion to the quantity of ferment present; this is shown by the following numbers, which I have arranged in tabular form:—

Hydrolysis of Castor Oil by means of Castor Seed Ferment, showing the Influence of the Quantity of Seed

Oil.	Grms.	Extracted Castor Seed.	Fatty Acids formed. Per cent.	After Hours:	Acid.
		Grms.			
Castor oil	5	0·5	89	24	5 grms. of 2 per cent acetic acid
			92	48	
,, ,,	10	0·5	81	24	10 ,, ,,
			86	48	
,, ,,	15	0·5	77	24	15 ,, ,,
			87	48	
,, ,,	20	0·5	71	24	20 ,, ,,
			80	48	
,, ,,	25	0·5	60	24	25 ,, ,,
			74	48	
,, ,,	50	0·5	49	24	50 ,, ,,
			49	48	
,, ,,	10	0·2	55	24	10 ,, ,,
			64	48	10 ,, ,,
			70	72	10 ,, ,,
			70	96	10 ,, ,,
			78	120	10 ,, ,,
			79	144	10 ,, ,,
			79	168	10 ,, ,,
			79	240	10 ,, ,,

The quantity of water used for emulsifying the fat influences favourably the amount of hydrolysis up to a certain extent,[4] as will be gathered from the following table:—

---

[1] *Bull. Soc. Chim.*, 1904 (31), 1194.

[2] *Zeits. f. phys. Chem.*, 1907 (50), 414.

[3] *Journ. of Biolog. Chem.*, 1906, ii. 89.

[4] Cp. Fokin, *Chem. Revue*, 1904, 119; 139; 169.

Hydrolysis of Castor Oil by means of Castor Seed Ferment, showing the Influence of the Quantity of Water

	Grms.	Castor Seed containing Oil.	Free Acids formed. Per cent.	After Hours:	Acid.
		Grms.			
Castor oil	6·5	5	68	3	2 grms. of 2 per cent acetic acid
			74	18	
			74	42	
,, ,,	6·5	5	74	3	4 ,, ,,
			80	18	
			84	42	
,, ,,	6·5	5	75	3	6 ,, ,,
			84	18	
			86	42	
,, ,,	6·5	5	76	3	8 ,, ,,
			87	18	
			85	42	
,, ,,	6·5	5	76	3	10 ,, ,,
			86	18	
			86	42	

For tables summarising similar experiments made by *Nicloux*, and detailing the influence of temperature, of the products of reaction, of the quantity of ferment present, and for the applicability to the enzymic hydrolysis of the general (logarithmic) law, $K = \frac{1}{t} \log. \frac{a}{a-x}$, as expressing correctly the velocity of the saponification, the reader must be referred to the original pamphlet.[1] With regard to the choice of the acid, it may be stated that the weaker the acid the more pronounced is the progress of hydrolysis. For a number of experimental results obtained with acetic, sulphuric, oxalic, phosphoric, tartaric, hydrochloric, nitric, hydrofluoric, and citric acids, as also with neutral and acid salts of calcium and magnesium, on different oils and fats, *Nicloux's* pamphlet must be consulted. With regard to the "activating" influence of these salts, especially of manganese sulphate, cp. Vol. III. Chap. XV. The statement that carbonic acid in seeds favourably influences the hydrolysis of the contained oil is confirmed by experiments of *Nicloux, Urbain*, and *Fokin*, whilst *Hoyer* maintains that carbonic acid is incapable of assisting hydrolysis.

Y. Tanaka[2] is of the opinion that the action of the dilute acid in the fermentative process of hydrolysis consists exclusively in converting an insoluble zymogen, present in the castor seed, into an active lipase, which is, like the zymogen itself, insoluble in water.

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[1] Maurice Nicloux, *Contribution à l'Étude de la Saponification des Corps Gras*, Paris, 1906; cp. also A. W. Visser, *Zeits. f. physik. Chemie*, 1905 (52), 257. H. Euler, (Hoppe-Seyler's *Zeits. f. physiol. Chem.*, 1905 (45), 420; *Zeit. f. d. gesam. Biochemie*, 1905 (7); *Zur Kenntniss der Katalasen*); A. E. Taylor, *Journ. of Biolog. Chem.*, 1906, ii. 87; H. E. Armstrong and E. Ormerod, *Proc. Roy. Soc.*, 1906 (78), 376; D. Sommerville, *Biochem. Journ.*, 1912 (6), 203; O. Loew, *Biochem. Zeits.*, 1911 (31), 159; L. Berczeller, *Biochem. Zeits.*, 1911 (34), 170; Y. W. Jalander, *Biochem. Zeits.*, 1911 (36), 435; K. F. Falk and T. M. Nelson, *Journ. Amer. Chem. Soc.*, 1912 (34), 735, 828.

[2] *Journ. of the College of Engin.*, Tokyo, 1910 (v.), 25.

On washing thoroughly the lipase, prepared by means of acid from castor seed, with water, so as to remove every trace of acid, the lipase still exhibits strong hydrolysing powers, without requiring the addition of any acid. Active lipase, therefore, is most effective in neutral solution, and is inhibited in its action by the presence of free acid, especially of free mineral acid. In an alkaline medium, lipase is inactive, and is less resistant to alkalis than the zymogen from which it originates.

Later experiments[1] showed that an optimum quantity of acid liberates the enzyme present as zymogen, and does not render the lipolytic medium acid. *Tanaka* prepares, therefore, an active "lipase powder" by triturating 100 grms. of extracted or expressed castor seed with 600-700 c.c. of 1/10 normal acetic acid or about 500 c.c. of 1/10 normal sulphuric acid at 30° to 35° C. for 30 minutes. The milky liquid is then filtered and the residue thoroughly washed with water and dried at a temperature not exceeding 40° C. The "lipase powder" thus obtained as an odourless, tasteless, white powder, is free from soluble matter. This preparation rapidly hydrolyses fats in the presence of water alone. *Tanaka* states that the "lipase powder" can be kept for a long time without materially losing its activity. He confirms the observations of previous observers (see above) as to the stimulating or, as the case may be, retarding influence of salts. Whilst confirming the stimulating effect of the manganese salt, he shows that it accelerates the hydrolysis in the first phase only. Glycerin acts as an inhibitor. The retarding influence of oxidised fatty acids is most pronounced in the case of polymerised and drying oils. *Tanaka* adds to the list of substances having a stimulating effect: leucine, asparagine, and similar decomposition products of proteins.

The technical application of hydrolysis with the aid of the castor seed ferment, and the attempts made hitherto to isolate the latter, will be described in Vol. III. Chap. XV. under "Preparation of Soap Stock Fatty Acids by the Ferment Process."

Ferments contained in other seeds do not as a rule exhibit the power of hydrolysing glycerides in the same pronounced manner. The seeds of *Hevea brasiliensis* (see Vol. II. Chap. XIV. "Para Rubber Tree Seed Oil") contain a powerfully acting enzyme. *Fokin*[2] studied the lipolytic action of a large number (60) of seeds. The ferment contained in *Chelidonium majus* appears to approach, as regards lipolytic activity, that of castor seed, whilst all others showed much weaker effects. *Fokin's* opinion[3] that all plants which contain lipolytic ferments are poisonous, cannot be admitted as being correct. It is much more reasonable to assume[4] that in all seeds in which fat is stored a ferment is contained which hydrolyses the fatty reserve material at the time it is required for the germinating embryo.

For the action of other lipolytic ferments, such as those contained in *Abrus precatorius* (*Braun and Behrendt*[1]) in fungi (*Zellner*[2]), in kola nut (*Mastbaum*[3]), in the seeds of *Croton Tiglium* (*Scurti and Parrozzani*[4]), of *Aesculus hippocastanum* (*Siegmund*[5]), of sweet almonds (*M. Tonegutti*[6]), the original papers given in the footnotes must be consulted.

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[1] *Journ. of the College of Engin.*, Tokyo, 1912 (v.), No. 4, pp. 125-152.

[2] *Chem. Revue*, 1904, 48, 69, 91; cp. also Schimanski, *Chem. Zeit.*, 1911, 1376.

[3] *Chem. Rev.*, 1906, 130.

[4] Cp. Lewkowitsch, *Jahrbuch der Chemie*, 1906, xvi. 307; Dunlap and Seymour, *Journ. Amer. Chem. Soc.*, 1905, 935.

The enzymes contained in animal organisms (*Claude Bernard*) appear to act much more slowly than those occurring in the seeds of plants. Thus the lipase contained in the liver, whilst it hydrolyses ethylbutyrate somewhat readily,[7] hardly attacks oils and fats; this has also been confirmed in the author's experiments.[8]

Steapsin, the ferment contained in the pancreas,[9] is, however, a comparatively powerful fat-hydrolysing ferment, as is proved by experiments made by the author in collaboration with *Macleod*.[10] The following table recapitulates some of the results which the author obtained with two steapsin preparations "1" and "2" furnished by *Macleod*:—

---

[1] *Berichte*, 1903, 1900.

[2] *Monatsh. f. Chem.*, 1906 (27), 295.

[3] *Chem. Revue*, 1907, 5.

[4] *Chem. Zeit.*, 1907, 229.

[5] *Monatsh. f. Chem.*, 1910 (31), 657.

[6] *Staz. Spar. Agr. Ital.*, 1910, 723.

[7] Kastle and Loevenhart, *Journ. Amer. Chem. Soc.*, 1900 (24), 49.

[8] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1903, 78. As to an explanation of the inactivity of the liver lipase cp. R. Magnus (*Zeits. f. phys. Chem.*, 1904 (42), 149); cp. also H. E. Armstrong, *Proc. Roy. Soc.*, 1905, 606; Bodenstein, *Chem. Zeit.*, 1906, 557.

[9] With regard to *pancreatic lipase* cp. O. Rosenheim and J. A. Shaw-Mackenzie, *Journ. Physiol.*, 1910 (xl.); cp. also P. Saxl, *Biochem. Zeits.*, 1908 (12), 343; C. A. Pekelharing, *Zeits. f. physiol. Chem.*, 1912 (81), 355. H. Davidsohn, *Biochem. Ztschr.*, 1912 (45), 284, is of the opinion that pancreas lipase differs in its action from a lipase occurring in the stomach. Cp. *Idem. Ibid.*, 1913 (49), 249.

[10] *Proc. Roy. Soc.*, 1903 (72), 31. Cp. also Lewkowitsch, *Report on V. Internat. Congress*, Berlin, vol. ii. p. 544; Fokin, *Chem. Rev.*, 1904, 244; Warburg, *Chem. Centralb.*, 1906 (ii.), 1784; E. Baur, *Zeits. f. angew. Chem.*, 1909, 97; E. F. Terroine, *Biochem. Zeits.*, 1910 (23), 404; E. Fernandez, *Chem. Zeit.*, 1910, 331; M. E. Pennington and J. S. Hepburn, *Journ. Am. Chem. Soc.*, 1912 (34), 210.

Hydrolysis with the aid of Steapsin Preparations

Preparation.	Cubic Centimetres of Preparation per 100 Grms. of Cotton Seed Oil or Lard.	Date on which started.	Added to Emulsion.		Percentage of Free Fatty Acids formed.					
			Acid.	Alkali.	Feb. 23.	Mar. 2.	Mar. 9.	Mar. 16.	Apr. 16.	May 1.
Cotton Seed Oil.										
1	20	19/2/03	0	0	22·9	...	43·3	48·4	80·6	...
1	30	19/2/03	0	0	32·8	...	49·9	60·45	86·7	...
1	25	19/2/03	0·5 c.c. of 2 per cent acetic acid	0	10·22	26·4	41·04	48·8	74·7	...
1	30	19/2/03	0	0·5 c.c. 1/10 norm. NaOH	31·25	39·5	55·4	63·1	...	...
2	30	5/3/03	0	0	...	...	37·1	44·3	68·3	70·2
2	50	5/3/03	0	0	...	...	32·7	46·4	71·5	83·8
2	60	5/3/03	0	0	...	...	31·03	46·3	60·8	79·5
2	60	5/3/03	0·5 c.c. of 2 per cent acetic acid	0	...	...	30·4	45·2	65·3	73·7
2	60	5/3/03	0	0·5 c.c. 1/10 norm. NaOH	...	...	36·5	44·9	66·4	73·5
2	30	5/3/03	0	1 c.c. 1/10 norm. NaOH	...	...	31·4	43·8	74·1	74·3
2	50	5/3/03	1 c.c. of 2 per cent acetic acid	0	...	...	37·66	44·5	65·2	77·2
Lard.										
2	50	5/3/03	0	0·5 c.c. 1/10 norm. NaOH	...	...	8·98	9·2	29·9	46·7
2	80	5/3/03	0	1 c.c. 1/10 norm. NaOH	...	...	12·2	14·4	20·7	22·9

Kanitz[1] states that by extracting with glycerol the pancreas of neat and pigs, preparations were obtained which hydrolysed olive oil within six hours to an extent of about 30 per cent.

The hydrolysis of the mixed triglyceride lecithin by means of steapsin has been mentioned above (p. 38).[2]

The difficulty and costliness of preparing animal ferments as compared with the facility with which any desired quantity of vegetable lipolytic ferments can be obtained, places the technical application of animal lipolytic agents outside commercial considerations.

It has been incidentally shown in the previous pages that hydrolysis does not readily reach completion, as the chemical reaction involved in hydrolysis is a reversible one; the products of hydrolysis thus have a tendency to recombine, and hence to reproduce again glycerides. By means of water, or concentrated sulphuric acid, or the *Twitchell* reagent, complete hydrolysis can be effected; in the case of water, by increasing the temperature and the time; in the case of the last two reagents, by increasing the quantity of the accelerator, as also the length of time during which the masses are allowed to react. With enzymes the progress of hydrolysis is also influenced by the mass of ferment present, but only to a certain extent, and, for practical reasons, it is obviously impossible to increase the proportion of ferment beyond a certain amount. Hence the reverse reaction can take place more readily. Whilst *Croft Hill*[3] is of opinion that all enzymatic processes are reversible, the author was unable to find any such action in the case of hydrolysis by means of steapsin. The small number of experiments made in this direction do not, however, permit general conclusions to be drawn; for *Pottevin's*[4] synthesis of mono-olein and tri-olein, as also *Taylor's* confirmation of the synthesis of triolein (whilst negative results were obtained in the case of palmitin and stearin), must be interpreted as proving that synthesis of glycerides, *i.e.* the reverse reaction, does take place even *in vitro*. Recently the evidence that the enzymatic hydrolysis is a reversible process has been confirmed by several experimenters.[5] Thus *Welter*[6] has shown that the synthesis of glycerides can be effected by means of the castor oil ferment at the ordinary temperature *in vitro*, and reach as high a percentage as 35, if the mixture of fatty acids, glycerin and ferment, is kept free from water as far as possible. Further, *A. Hamsik*[7] has shown that pancreas lipase is capable of effecting the synthesis of palmitin and stearin from glycerol and palmitic and stearic acids respectively. Moreover, there can be no doubt that in the animal organism there occurs a rhythmic play of enzymatic hydrolyses and syntheses of fats, according to the local requirements of the organs, for on no other assumption [1] is it possible to explain satisfactorily the influence of food on the composition of the milk fat of mammals (cp. Vol. II. Chap. XIV. "Animal Fats"). The synthesis of glycerides by means of *Twitchell's* reagent has been shown above (p. 7) to be feasible on a practical scale.

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[1] Hoppe-Seyler's *Zeits. f. physiol. Chem.*, 1905 (46), 482; cp. also A. Fromme, *Zeits. f. die gesamte Biochem.*, 1905, 51.

[2] Cp. also Schumoff-Simanowski and N. Sieber, *Zeit. f. physiol. Chem.*, 1906 (49), 50.

[3] *Journ. Chem. Soc.*, 1894, 634.

[4] Cp. *Annal. de l'Inst. Pasteur*, 1906, 901.

[5] For further references to the literature of fermentative synthesis (mostly of a strictly physiological character) cp. A. E. Taylor, *Journ. of Biolog. Chem.*, 1906, ii. 89, p. 587.

[6] *Zeits. f. angew. Chem.*, 1910 (24), 385; cp. also W. Dietz, *Zeits. physiol. Chem.*, 1907 (52), 279; F. L. Dunlap and L. O. Gilbert, *Journ. Amer. Chem. Soc.*, 1911 (33), 1787; S. Iwanow, *Berichte d. deutsch. botan. ges.*, 1911 (29), 595.

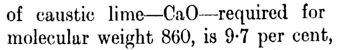
[7] Hoppe-Seyler's *Zeits. f. physiol. Chem.*, 1911 (71), 238; cp. also M. Krausz, *Beiträge zur fermentativen Fettspaltung*, Pécs, 1910.

Thus the analogy pointed out above as existing between the catalytic action of the *Twitchell* reagent and that of the castor seed ferment may be expanded into the statement, that they are both able to effect, under suitable conditions, synthesis as well as hydrolysis, much in the same manner as platinum black [2] is capable of acting as an accelerator both in hydrolysing and synthesising glycerides.

Another class of accelerating agents which are employed on a very large scale are *basic materials*, such as zinc oxide, magnesium oxide, calcium oxide, and especially the caustic alkalis.

If the view that the bases act as accelerating agents, in other words as catalysts, be correct, it should not be imperative that the bases be present in at least molecular proportion to the fatty acids that will result on complete hydrolysis. The greater the amount of the bases present, the more rapidly should the resolution of the glycerides into their components take place, and the greater should be the amount of salts of the fatty acids formed. But a deficiency of the bases necessary to neutralise all the fatty acids obtainable by complete hydrolysis should not preclude the completion of hydrolysis.

Since the velocity of saponification stands in direct ratio to the quantity of the bases, then, in the presence of an excess of bases, it should be possible to lower the temperature and shorten the time required for effecting practically complete hydrolysis. These views are confirmed by the practice of the technical process of *saponifying* (hydrolysing) *by means of lime*. The quantity of lime required to neutralise the fatty acids produced on completely hydrolysing a glyceride can be calculated from the following summarising equation :—

(4) 

$$2C_3H_5\underset{OR}{\overset{OR}{OR}}+3Ca(OH)_2=2C_3H_5\underset{OH}{\overset{OH}{OH}}+3Ca(OR)_2.$$

The amount of caustic lime—CaO—required for a triglyceride having the mean molecular weight 860, is 9·7 per cent, but even prolonged boiling with steam in an open vessel with that proportion of lime will not lead to complete saponification. Unless the proportion of caustic lime be raised to 12-14 per cent, the hydrolysis of the glyceride cannot be brought to an end in an open vessel, *i.e.* at a temperature of from 100° to 105° C. (cp. Vol. III. Chap. XV.). If, however, the temperature be raised (as is done on a large scale by treating fats with milk of lime in an autoclave under pressure; see Vol. III. Chap. XV.), the proportion of caustic lime can be reduced gradually, until, at a pressure of 12 atmospheres (corresponding to a temperature of 190° C.), even 1 per cent of lime suffices for practically complete hydrolysis. Although the glyceride is completely hydrolysed, only so much of the fatty acid is neutralised by lime, *i.e.* converted into lime soap, as is chemically equivalent to the quantity of lime employed.

---

[1] This view does not, of course, postulate that there should be present in the tissues an amount of lipase proportional to the amount of fat deposited in the tissues (cp. H. C. Bradley, *Journ. Biol. Chem.*, 1913 (13), 407).

[2] C. H. Neilson, *Amer. Journ. of Phys.*, 1904 (10), 191. G. Bredig., *Centralb. f. Bakter., Parasit. u. Infect.*, 1907 (xix.), 485.

The same considerations—*mutatis mutandis*—hold good if zinc oxide, magnesium oxide, or caustic alkalis are used as accelerators. In the last case, hydrolysis proceeds much more rapidly, inasmuch as in contradistinction to hydrolysis accelerated by lime, a water-soluble soap is formed, which helps to emulsify the fats. There can be no doubt that under pressure complete hydrolysis would be brought about by an amount of caustic alkali insufficient to neutralise all the fatty acids formed. On a large scale, for obvious reasons, such a process is not employed. The compounds resulting from the combination of fatty acids and caustic alkalis being useful commercial products—soaps—the aim of the manufacturer is to conduct operations in such a manner that these products are obtained concurrently with the hydrolysis of the fats. Hence, on a commercial scale oils and fats are boiled in open vessels with a solution of caustic alkali, containing not only sufficient alkali to neutralise all the fatty acids obtainable on hydrolysing the glycerides, but also an excess whereby also the time required for the completion of the reaction is shortened. Indeed, this excess of alkali is necessary in order to complete the reaction and to do so in the shortest possible time.

In accordance with the law of mass action, the velocity of the reaction will be great at the beginning and will gradually slow down until an equilibrium is established between the tendency of alkali to neutralise the acids, on the one hand, and the opposite tendency of water to dissociate the soap formed, on the other. Hence, under the given conditions of temperature and pressure, an equilibrium will be established very rapidly, beyond which no further progress of the reaction in either direction will occur.

This is clearly brought out by the following experiments carried out in my laboratory by *Clapham* and by *de Greiff*: [1]—

(1) 2000 grms. of tallow were "boiled" by means of open steam, as in the method employed on a large scale, with 282 grms. of pure caustic soda—the theoretical quantity required to neutralise the fatty acids obtainable. The boiling was continued beyond the time required on a manufacturing scale. The pasty soap gave on examination the following result:—

---

[1] Cp. third edition of this work, Vol. I. p. 53, and Lewkowitsch, "Modern Views on the Constitution of Soap," *Journ. Soc. Chem. Ind.*, 1907, 590.

	Per cent.
Total fatty matter	33·00
Total alkali	3·708
Fatty acids as soap	31·01
Combined alkali as soap	3·496
Unsaponified fat	2·0
Free alkali	0·212

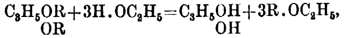
This experiment shows that only 94 per cent of the tallow was saponified. On adding an excess of alkali, the equilibrium between the reacting masses is changed in the direction of a greater amount of soap being formed, so that by employing a suitable excess—as is done on a large scale—complete hydrolysis of the fat, followed immediately by complete neutralisation of the fatty acids, is obtained.

(2) 3000 grms. of safflower oil (of the saponification value 192·37) were boiled in a similar fashion with a solution containing 412·2 grms. of sodium hydroxide. After the whole amount of caustic soda had been added, a sample of the mass taken out of the soap-kettle showed the following composition :—Fatty matter, 29·23 per cent (consisting of fatty acids, 25·18 per cent ; unsaponified oil, 4·05 per cent) ; total alkali, 3·09 per cent (consisting of combined alkali, 2·86 per cent ; free alkali, 0·23 per cent) ; or, calculated to 100 parts : Fat saponified, 86·14 per cent ; fat unsaponified, 13·86 per cent ; alkali combined, 92·56 per cent ; alkali free, 7·44 per cent.

The remainder of the fatty mass was boiled for a somewhat longer period, and the curd thrown up by salt. The curd contained : Fatty matter, 60·10 per cent (consisting of combined fatty acids, 54·92 per cent ; unsaponified fat, 5·18 per cent) ; total alkali, 6·59 per cent (consisting of combined alkali, 6·26 per cent ; free alkali, 0·33 per cent) ; or, calculated to 100 parts : Fat saponified, 91·36 per cent ; fat unsaponified, 8·64 per cent ; alkali combined, 95 per cent ; alkali free, 5 per cent.

From the foregoing it will be evident that for *analytical* purposes the most rapid method for hydrolysing fats consists in using caustic alkalis. Since, however, even the employment of an excess of alkali in aqueous solution entails a very lengthy operation, which is not always carried out successfully by an analytical chemist without some practical experience in soap-making, it is necessary to accelerate hydrolysis still further in the *laboratory*. This is done by employing caustic alkalis in strong ethylalcoholic (or amylalcoholic) solution.

The action of caustic soda in alcoholic solution need not be considered as differing, theoretically, from hydrolysis in aqueous solution, if we look upon alcohol as water in which one hydrogen atom is replaced by the group C_2H_5 (or C_5H_{11}).[1] Ignoring for a moment the alkali, the hydrolysis would proceed according to the following equation—

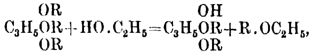
(5) 

$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix}+3H.OC_2H_5=C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}+3R.OC_2H_5,$$

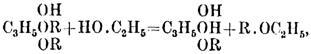
---

[1] Cp. *Science*, December 9, 1904, New York (Lewkowitsch) ; cp. also above, p. 71.

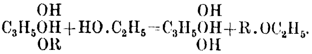
which should again be looked upon as summarising the following three equations :—

(5*a*) 

$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix}+HO.C_2H_5=C_3H_5\begin{matrix}OH\\OR\\OR\end{matrix}+R.OC_2H_5,$$

(5*b*) 

$$C_3H_5\begin{matrix}OH\\OR\\OR\end{matrix}+HO.C_2H_5=C_3H_5\begin{matrix}OH\\OH\\OR\end{matrix}+R.OC_2H_5,$$

(5*c*) 

$$C_3H_5\begin{matrix}OH\\OH\\OR\end{matrix}+HO.C_2H_5=C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}+R.OC_2H_5.$$

The resulting products would be glycerol and ethylic esters of the fatty acids. Although the feasibility of these reactions had not been tested experimentally, the author [1] had expressed the opinion that with anhydrous materials and under high pressure,[2] especially if assisted by a suitable catalyst,[3] the reaction would very likely proceed a long way in the direction indicated by the equation (5).

This prediction has been realised in the method of *Haller*,[4] who employs as a catalyst hydrochloric acid (cp. p. 79). *Haller* warms one part of oil or fat with two parts of alcohol (methyl alcohol,[5] ethyl alcohol,[5] or propyl alcohol) containing 1 to 2 per cent of hydrochloric acid,[6] until a homogeneous mixture is obtained. The chemical change is expressed by equation (5). According to the alcohol employed, methyl-, ethyl-, or propyl-esters of the acid radicle originally contained in the glycerides are formed. The glycerol obtained simultaneously can be removed by washing the product of the reaction with water. The application of this method of hydrolysis, which has been termed by *Haller* " alcoholysis " (and in especial, according to the alcohol employed, " methanolysis," " ethanolysis," " propanolysis "), to the examination of oils and fats [7] will be considered in Chapter XII.

A catalyst, which behaves in a manner similar to that of hydrochloric acid, is, according to *Haller*, phenolsulphonic acid. The similarity of the latter to the *Twitchell* reagent renders it very likely that the *Twitchell* reagent also would act as a catalyst in alcoholic solution.

In the absence of water the chemical change cannot proceed beyond the formation of ethyl esters. But if the alcohol contain water, the ethyl esters in their turn are hydrolysed by the water to some extent. Complete hydrolysis, as indicated by the following equation—

$$(6)\ 3C_2H_5.OR+3H.OH=3R.OH+3C_2H_5.OH,$$

---

[1] *Journ. Soc. Chem. Ind.*, 1903, 595.

[2] This idea has been patented by Dreymann: English patent 10,466, 1904, German patent 164,154.

[3] Cp. Lewkowitsch, "Problems in the Fat Industry," *Journ. Soc. Chem. Ind.*, 1903, 595.

[4] *Compt. rend.*, 1906 (143), 657 ; cp. also French patent 361,552.

[5] Similar experiments have been carried out before Haller by Rochleder, *Liebig's Annal.*, 1846 (49), 260 ; Berthelot, *Ann. de Chim. et de Phys.*, 1854 (41), 3rd série, 311 ; and *Chim. organ.* vol. ii. 81.

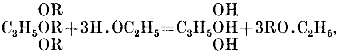
[6] With a view to avoiding possibility of oxidation Rollett adds tin.

[7] Lecithin and other lipoids are also readily hydrolysed by the same method. Cp. E. Fourneau and M. Piettre, *Bull. Soc. Chim.*, 1912 (iv.), 805.

cannot result, since an equilibrium between ester, water, and free fatty acids would soon be established. (It may be pointed out that in "alcoholysis" the change is not a complete one.) The reaction thus arrested will, however, proceed if alkali be present to neutralise the free acid formed. Since in laboratory operations caustic alkali is added to the alcohol in a quantity greater than that which is chemically equivalent to the fatty acids, the fatty acids formed (according to equation (6)) will be immediately neutralised, as is shown by the following equation :—

$$(7)\ 3R.OH+3Na.OH=3Na.OR+3H.OH.$$

Hence the chemical change represented by equation (6) will become complete. By adding the three equations (5), (6), and (7)—

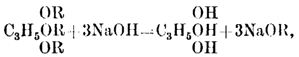
(5) 

$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix}+3H.OC_2H_5=C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}+3RO.C_2H_5,$$

$$(6)\ 3R.OC_2H_5+3H.OH=3R.OH+3H.OC_2H_5,$$

$$(7)\ 3R.OH+3Na.OH=3Na.OR+3H.OH,$$

we obtain as the final result :—



$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix}+3NaOH=C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}+3NaOR,$$

which is identical with the above given equation (3).

The correctness of the views I have given here is confirmed by a number of observations. Thus *Duffy* has shown that tristearin, on being boiled with a solution of sodium in absolute alcohol, is partly converted into ethyl stearate. *Bouis* also demonstrated that ethyl stearate is formed on heating tristearin, dissolved in ether, with small quantities of alcoholic potash, and he further showed that the total amount of glycerol was split off, the chemical change taking place in the course of one or two minutes. *J. Bell* found that on boiling butter fat with half the quantity of alcoholic potash required for complete saponification, a light oil is obtained, which solidifies at 43° C. This oil, judged by him to be a diglyceride of the composition $C_3H_5(OH)(OC_{16}H_{31}O)(OC_{18}H_{33}O)$, was actually a mixture of ethyl esters of fatty acids. Similarly *Allen*[1] ascertained that on heating acetin with one-fiftieth part of the alcoholic potash required for complete saponification, 39 per cent of the theoretically possible quantity of ethyl acetate had been formed, whilst three-fiftieth parts of potash converted 85 per cent into acetic ester. If a larger proportion of alkali was employed, the yield of acetic ester decreased ; thus with sufficient caustic soda to saponify 39·8 per cent of the acetin used, the amount converted into acetic ester was 52·4 per cent. The formation of ethylic esters on saponifying mutton tallow with sodium alcoholate was demonstrated by *Kossel and Krüger*.[2] *Henriques*[3] confirmed the foregoing experiments by again proving that if an insufficient amount of alkali be used, the chemical change taking place consists in the complete splitting off of glycerol with formation of ethylic esters (or methylic, or amylic esters, according as methyl-alcohol or amyl-alcohol was substituted for ethyl alcohol). Thus he showed that in the case of linseed, rape, almond, olive, and castor oils, the complete conversion of the glycerides into ethylic esters took place when only 33·3 or 25 or 15 per cent of the theoretical amounts of alkali was employed ; in the case of castor oil, even 10 per cent was found to be sufficient. The " alcoholysis " as effected by *Haller's* method must be considered the final proof supplementing in a welcome manner the isolated observations enumerated above.[1]

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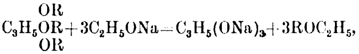
[1] *Chem. News*, 1891, 64 ; 179.

[2] *Zeits. f. phys. Chem.*, 1891 (15), 321.

[3] *Journ. Soc. Chem. Ind.*, 1898, 673, 853 ; *Zeits. f. angew. Chem.*, 1898, 697.

The foregoing views rest on the fundamental principle that water (or in modern parlance the OH ion) is the true hydrolysing agent, and that in the absence of water the reaction cannot proceed to the formation of glycerol. Since for the hydrolysis of 1 grm. of fat no more than 0·06 grm. of water is required, the fact that it is difficult to keep out traces of water from alcohol (especially whilst it is being boiled with the fat under examination) satisfactorily disposes of a number of experiments purporting to show that saponification will take place in the absence of water. Such experiments were first carried out with sodium alcoholate (sodium ethoxide, C_2H_5ONa) by *Bouis*[2] and by *Duffy*. Later on *Kossel and Obermüller*[3] suggested the same method as the quickest and surest means of saponifying fats completely in the laboratory ; and *Kossel and Krüger*[4] stated that in a number of experiments with sodium ethoxide, saponification was complete if the theoretical quantity of sodium was employed. Since the reaction must take place according to the following equation—

(8) 

$$C_3H_5\begin{matrix}OR\\OR\\OR\end{matrix}+3C_2H_5ONa=C_3H_5(ONa)_3+3ROC_2H_5, \tag{8}$$

it is difficult to see how glycerol can be formed in the absence of water. *Obermüller*, later on, removed the difficulty by the statement that in the foregoing experiments the last traces of water had not been excluded rigorously, so that the sodium glyceroxide obtained according to the above equation was readily decomposed by water, with the formation of glycerol and sodium hydrate. The sodium hydrate thus set free could then react with the more readily saponifiable ethylic esters, and their saponification was rapidly completed on boiling. He further showed that if carefully dried alcohol was used for saponification, and access of moisture from the atmosphere was prevented by means of calcium chloride, about 30 per cent of fat remained unsaponified. Considering the extreme difficulty of excluding the last traces of moisture (calcium chloride is incapable of effecting this completely !), the conditions under which even these experiments were carried out do not preclude the assumption that traces of moisture had effected the saponification of two-thirds of the fat.

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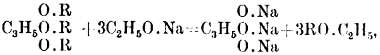
[1] The observation of Hanus (*Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 581) that arachis oil and mace butter give no homogeneous solution with alcoholic potash, requires confirmation.

[2] *Compt. rend.*, 1857 (45), 35.

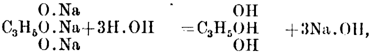
[3] *Zeits. f. physiol. Chem.*, 1891 (15), 321-330.

[4] *Ibid.*, 1891 (15), 322.

The complete saponification of fats by means of sodium ethoxide, resulting in the production of glycerol and sodium salts of fatty acids, must therefore be symbolised by the following three equations :—

(9) 

$$C_3H_5\begin{matrix}O.R\\O.R\\O.R\end{matrix}+3C_2H_5O.Na=C_3H_5\begin{matrix}O.Na\\O.Na\\O.Na\end{matrix}+3RO.C_2H_5,$$

(10) 

$$C_3H_5\begin{matrix}O.Na\\O.Na\\O.Na\end{matrix}+3H.OH=C_3H_5\begin{matrix}OH\\OH\\OH\end{matrix}+3Na.OH,$$

$$(11)\ 3R.OC_2H_5+3Na.OH=3H.OC_2H_5+3Na.OR.$$

These three equations represent three consecutive chemical changes, each of which in its turn must be considered as a summary of three reactions, such as are represented by equations (1*a*), (1*b*), and (1*c*), and equations (5*a*), (5*b*), and (5*c*).

Although for many purposes, especially for the subsequent estimation of glycerol, it would be more convenient in the laboratory to use for saponification such bases as will form insoluble salts with the fatty acids (for instance, lead oxide,[1] lime, and baryta), they must be rejected, as saponification by means of these bases is not complete. Therefore in all analytical operations caustic alkalis must be employed if reliable results are to be obtained.

Caustic potash is preferable to caustic soda, since potash soaps are more readily soluble than soda soaps ; the more intimate contact of the reacting masses thus helps to bring the saponification more rapidly to an end. Although the theoretical amount required for 1 grm. of fat is from 0·19 to 0·26 grm. of caustic potash, a considerable excess is necessary to ensure complete saponification in a short time.

The following are convenient proportions for saponifying oils and fats in the laboratory :—To 10 parts of oil or fat, weighed off in a flask, are added 30 to 40 parts of alcohol [2] by volume, and 4 to 6 parts of

[1] Processes of saponification by means of lead oxide are claimed in English patents 1033, 1887 ; 18,163, 1895 ; cp. also Schrauth, *Augsburger Seifensieder Zeit.*, 1908, 442.

[2] If the cost of spirits of wine preclude its use, recourse may be had to methylated spirit. This alcohol may be purified for analytical purposes by the following method, proposed by Waller (*Journ. Amer. Chem. Soc.*, 1889, 124 ; *Analyst*, 1890, 50) :—The alcohol is shaken with powdered potassium permanganate until it assumes a distinct colouration. It is then allowed to stand for some hours until the permanganate has been decomposed and hydrated manganese peroxide has settled. A pinch of calcium carbonate is then added, and the alcohol distilled from a flask, provided with an efficient fractionating column. The distillate is tested frequently until 10 c.c., when boiled with 1 c.c. of a strong (syrupy) solution of caustic potash, give no yellow colouration on standing for twenty or thirty minutes. What distils after that is preserved for use ; care, however, must be taken not to distil to dryness. The alcohol thus prepared is completely neutral, and is especially suitable for the preparation of alcoholic potash solution ; even on standing for a long time alcoholic potash made from such alcohol does not become dark coloured.

Another method recommended by J. Carter Bell (*Journ. Soc. Chem. Ind.*, 1893, 236) is as follows : 500 c.c. of methylated alcohol, of about 85 or 90 per cent, are placed in a flask of about 1000 c.c. capacity, with 25 grms. of stick potash. When the latter has dissolved, 250 grms. of melted lard (or of some other saponifiable fat) are added. The flask is then connected with an inverted condenser and heated on the water-bath, so as to saponify the fat. Then the condenser is reversed, and about 450 c.c. of alcohol solid caustic potash previously dissolved in 20 parts of water. The flask is then connected with an inverted condenser, and the contents are kept gently boiling for half an hour or an hour. These proportions may be varied within very wide limits. Thus *Yssel de Schepper and Geitel* recommend 20 grms. of fat, 40 c.c. of caustic potash of specific gravity 1·4, and 40 c.c. of alcohol, whilst *Dalican* proposes to pour, with constant shaking, a mixture of 40 c.c. of caustic soda, specific gravity 1·33, and 33 c.c. of 95 per cent alcohol (cp. also Chap. VI. "Saponification Value") into 50 grms. of fat previously heated to 100° C.

As commercial alcohol is seldom free from traces of acid, it should be tested for acidity, and if necessary, be neutralised with decinormal caustic alkali, using phenolphthalein as an indicator; or the alcohol may be distilled over lime or baryta immediately before use. For the purposes of analysis, rectified spirits of wine will, as a rule, be sufficiently pure. It should be examined by boiling a few c.c. with several drops of concentrated caustic potash; pure alcohol will not become brown; a slight yellow colour may, however, be allowed to pass. The appearance of a brown colour would point to the presence of aldehyde or acetone.

In order to accelerate the process of saponification, *Yssel de Schepper and Geitel*[1] add some ether, with a view to ensuring a readier contact of the particles of fat and alkali. This proposal has been repeated by

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are distilled off. According to Carter Bell, the alcohol thus obtained will not turn brown on the addition of potash after several days, and when the solution is kept in a strong light only a slight yellow colour may develop.

The property of soap, to retain the impurities of methylated spirit, is well known to manufacturers of transparent soap who dissolve stock soaps in boiling methylated spirit. The commercial methylated spirit when *first* used for this process yields a distillate which has a much less unpleasant smell than the crude spirit. At each subsequent time of using the methylated spirit a further improvement of the quality of the alcohol takes place; ultimately a spirit is obtained which is quite free from the rank odour of the commercial article. Kadel (*Pharm. Journ. and Transactions*, 1894, 356) distils impure alcohol first over caustic soda—30 grms. for 5 litres—after allowing to stand for a few days. The distillate is next treated with permanganate and distilled off again. If necessary, the latter operation is repeated and followed by filtration over charcoal. Dunlap (*Journ. Amer. Chem. Soc.*, 1906, 395), modifying L. W. Winkler's proposal (*Berichte*, 1905, 3612) to remove aldehydes by means of silver oxide, prepares aldehyde-free alcohol as follows: 1·5 grms. of silver nitrate dissolved in 3 c.c. of water are added to 1000 c.c. of 95 per cent alcohol in a glass-stoppered cylinder and mixed thoroughly. Three grms. of potassium hydroxide (pure by alcohol) are dissolved in 10-15 c.c. of warm alcohol, and, after cooling, are slowly poured into the alcoholic silver nitrate solution, taking care that the latter is not shaken. The precipitate of finely divided silver oxide slowly distributes itself through the contents of the cylinder, and settles completely after standing for some time. The clear supernatant liquid is syphoned off (or filtered off) and distilled. No portion of the distillate need be rejected.

It should be noted that in this country alcohol in which retailers are permitted to deal is methylated at present (General Order as to Methylated Spirit, July 20, 1891) by mixing "ordinary" methylated spirits (*i.e.* alcohol "denatured" with wood-naphtha to the extent of one-ninth of its volume) with 0·375 per cent of mineral naphtha (petroleum) of a specific gravity of not less than 0·800. This kind of methylated spirit is known as "mineralised methylated spirits." The admixed hydrocarbons are not removed by the foregoing processes of purification, as they pass over into the distillate with the alcohol. In estimations of "unsaponifiable matter" in fats this source of error must be specially guarded against.

[1] *Dingl. Polyt. Journ.*, 245, 295.

Hehner, *Duclaux*, and others; but I do not recommend it, as the presence of ether necessitates a lower temperature than would be required in some cases. *Henriques*[1] proposed a method of "cold saponification" which consists in dissolving the fat in petroleum ether and mixing the solution with alcoholic soda; on standing for twelve hours, complete saponification takes place. In addition to the disadvantage that an operation which can be easily finished in half an hour is unduly protracted, this method has the further drawback that the solution of alkali must be prepared with strongest alcohol, as it is essential to obtain a homogeneous liquid on mixing the alcoholic soda with petroleum ether. If alcoholic soda be employed, some sparingly soluble soda soaps may separate, and, by occluding unsaponified fat, prevent complete saponification. Although there is no reason why alcoholic potash should not be used in place of alcoholic soda to obviate the last-named difficulty, the considerable length of time required would still militate against the employment of this method in place of the usual one. In the case of sulphurised (vulcanised) oils and fats, however, the cold saponification process may be used with advantage, as by boiling with alcoholic potash sulphur is eliminated from the fatty substance to a far greater extent than when working in the cold. It may also be employed usefully in those special cases where it is intended to study the progress of saponification by analytical or physico-chemical methods.

With regard to the question as to whether the different triglycerides are saponified with equal facility, no definite conclusion has been reached at present. It has been stated that olein is hydrolysed with greater difficulty than palmitin or stearin. This statement has even led to the patenting of a process[2] for obtaining olein from olive oil (which consists essentially of olein and palmitin) by shaking the oil with caustic soda in the cold, when palmitin is said to be saponified, whereas olein is said to remain unchanged. Against this must be set the statement by *Thum*[3] that there is no marked difference between oleic and commercial stearic acids in their behaviour with caustic alkalis. On adding to a mixture of oleic and commercial stearic acids an amount of caustic potash insufficient completely to neutralise the fatty acids, the composition of the acids that had been converted into soaps was found to be almost the same as that of the acids that had remained free. Hence it is impossible to effect a separation of solid from liquid fatty acids by partial saturation with alkali. Conversely, *Henriques*[4] showed that on saponifying glycerides with amounts of caustic alkali, insufficient to neutralise all the fatty acids formed, no selective action of the alkali on the several glyceryl esters could be observed. However, inasmuch as saponification took place somewhat rapidly in these cases, the conclusions must be accepted with reserve.

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[1] *Journ. Soc. Chem. Ind.*, 1896, 299, 476. The objections raised by Henriques to the usual method of saponification are groundless (cp. Holde, *Journ. Soc. Chem. Ind.*, 1896, 476).

[2] German patent 37,397.

[3] *Zeits. f. angew. Chem.*, 1890, 482.

[4] *Journ. Soc. Chem. Ind.*, 1898, 673, 853; *Zeits. f. angew. Chem.*, 1898, 338, 697.

The subject has not yet been so completely investigated as it deserves, and it will only be possible to arrive at definite conclusions if hydrolysis is brought about very slowly. *Henriques'* methods of cold saponification, or hydrolysis in alcoholic solution assisted by hydrochloric acid, or hydrolysis by means of ferments, offer suitable methods for this purpose. The above-detailed experiments with steapsin would seem to show that cotton seed oil is much more easily hydrolysed than lard. *Haller*[1] is of opinion that the glycerides of the lower fatty acids are more readily hydrolysed than glycerides of higher fatty acids. The ready solubility of castor oil in alcohol satisfactorily explains the fact why by *Haller's* method this oil is more easily hydrolysed than glycerides which are insoluble in alcohol.

The fact that fats containing notable amounts of volatile fatty acids (cocoa nut oil, palm nut oil) lend themselves more suitably to the manufacture of "cold soap" (cp. Vol. III. Chap. XV. "Soap-making by the Cold Process") would also appear to speak in favour of the view that glycerides of lower fatty acids are more readily hydrolysed than those of the higher fatty acids, but it should be pointed out that in this case the caustic soda solution used must be of high strength. Experiments in this direction with pure triglycerides have not yet been carried out; these seem to be all the more required, as *Urbain, Saigon, and Feige*,[2] from their experiments with castor seed ferment, derived the conclusion that the saponification of the various glycerides appears to proceed at the same rate.

Those fats which are not saponified readily are best heated with alcoholic potash under pressure. The author proposed for this purpose a copper bottle with a screw-stopper; this bottle may be immersed in water, as it is not liable to breakage (as seltzer-water bottles are).

Carbonates of the alkalis do not saponify oils and fats under the same conditions as do caustic alkalis;[3] nor do silicates effect saponification. All statements[4] made to the contrary must be accepted with the greatest reserve.

Saponification of Waxes

In the case of waxes we have to deal with simple esters; hence hydrolysis (saponification) in stages cannot take place. The hydrolysis of waxes leads to the production of fatty acids and alcohols. Since the latter are insoluble in water (in contradistinction to glycerol), and therefore serve similar technical purposes as do the fatty acids themselves, waxes are not hydrolysed generally for the mere production of fatty acids and alcohols (cp. Vol. III. Chap. XV. "Technology of Waxes"). Hence a discussion of the methods of hydrolysis would serve no useful purpose; it need therefore only be pointed out that hydrolysis by means of water at high temperatures and pressures (superheated steam) is employed on a large scale as an intermediate process only, the temperature being kept so high that further changes with the production of hydrocarbons take place (cp. Vol. III. Chap. XV. "Montan Wax"; Vol. III. Chap. XVI. "Wool Fat"). Hydrolysis with the aid of the castor seed ferment seems to have been effected in the case of spermaceti up to a certain extent, but as this process has no practical importance, it need only be stated that in a semi-large scale experiment 32 per cent of spermaceti was hydrolysed (cp. German patent 145,413).

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[1] *Compt. rend.*, 1906 (143), 660.

[2] *Bull. Soc. Chim.*, 1904 (31), 1194.

[3] Bennet and Gibbs in 1865 claimed the saponification with alkali carbonate, but the formation of soap can only have been a secondary process, as hydrolysis seemed to have been brought about by the high temperature and pressure to which the glycerides were exposed (in presence of carbonate). Nor can M. Doyon and A. Morel's statement (*Compt. rend. Soc. Biolog.*, 1902 (54), 1524) that sodium carbonate, even in dilute solution, effects saponification at body temperature, be accepted without reserve; the monobutyrin with which they worked was most likely hydrolysed by water. Cp. also French patent 376,122 (E. de Grousseau).

[4] French patent 339,154 (C. Jourdan); English patent 27,280, 1906 (W. N. Bacon). Cp. also Scheurer-Kestner, *Compt. rend.*, 1860 (51), 317.

By saponifying waxes with alkali the salts of fatty acids and higher alcohols are obtained. Thus, myricin is resolved into the palmitate of the alkali metal and myricyl alcohol, according to the following equation:—

$$C_{15}H_{31}CO.O.C_{30}H_{61}+KOH=C_{15}H_{31}CO.OK+C_{30}H_{61}.OH.$$

On diluting the alcoholic solution of a saponified wax with water, the higher alcohols (being insoluble in water) separate out and rise to the surface of the liquid, or remain suspended in it, causing turbidity of the liquid. They are separated from the soap by shaking with ether, or by evaporating the solution together with the insoluble matter to dryness, and exhausting with petroleum ether (cp. Chap. IX. "Unsaponifiable Matter"). In practice the extracted substances, being insoluble in water and alkalis, are termed "unsaponifiable."

On saponifying beeswax and carnaüba wax it is necessary to employ strong alcoholic potash made with at least 96 per cent alcohol, and it is advisable to add to the alcoholic potash some absolute alcohol so as to ensure proper solution of the soaps formed. One hour's boiling is then sufficient to saponify the above-named waxes.

Wool wax must be boiled with an excess of half-normal alcoholic potash for at least twenty hours. It is, however, easily saponified by means of sodium in a solution of absolute alcohol (*Kossel and Obermüller's* method). The reagent (which must be made afresh for each series of experiments) is prepared by dissolving 5 grms. of metallic sodium or preferably potassium in 100 c.c. of absolute alcohol. The author has shown [1] that equally satisfactory results are obtained by saponifying with double normal alcoholic potash under pressure.[2]

The difficulty which the saponification of some of the solid waxes presents is no doubt due to the fact that the sodium soaps formed are less readily soluble than those obtained when saponifying fats. Thus in the case of wool wax,[1] *Lewkowitsch* has shown that the soaps are very sparingly soluble in water. Such soaps would naturally envelop unsaponified wax and thus protect it from contact with alkali. Therefore petroleum ether boiling above 120° C., suggested in *Henriques'* method of cold saponification, ensuring, as it does, a readier contact of alkali with wax, accelerates the reaction, especially so when the solution is heated. The alcoholic potash should be prepared with strongest alcohol. In the case of spermaceti, which yields easily soluble soaps, saponification is as readily effected as in the case of oils and fats.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 137.

[2] Henriques' statement that under these conditions the alkali acts on the alcohols contained in the wool fat with the production of acids is unfounded. Henriques' objections to the usual methods of saponification are likewise groundless (cp. Holde, *Journ. Soc. Chem. Ind.*, 1896, 476).

In order to be able to work at a higher temperature than is possible with ethyl alcohol, some operators employ amyl alcohol (propyl alcohol also has been proposed with the same object in view; cp. Vol. II. Chap. XIV. " Beeswax ").

Sundwick states that in the case of psylla wax (see Vol. II. Chap. XIV.) hydrolysis is more readily effected by means of hydrobromic acid than by means of alcoholic potash.

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[1] Fahrion states that wool grease (the proportion of free fatty acids is not stated) may be completely saponified on a water-bath in an open capsule by means of double normal alcoholic soda. The soap solution must be stirred constantly, evaporated down to dryness, and *repeatedly* taken up with strong alcohol to drive off the last traces of water, then again boiled down to dryness, and kept for some time on the water-bath. This is evidently not a very expeditious process (*Zeits. f. angew. Chem.*, 1898, 268).

CHAPTER III

CONSTITUENTS OF FATS AND WAXES

In this chapter only those acids and alcohols can be considered fully which are constituents of natural oils, fats, and waxes, or are derived from them by technical processes or, at least, stand in such near relationship to them that their description becomes necessary from a technological point of view. Those fatty acids and alcohols which have not been found in natural oils, fats, and waxes, or have not been shown to be derived from those technical products which form the subject of the third volume of this work, fall outside the scope of this chapter. Therefore isomerides of fatty acids which do not occur in nature will only be dealt with in the briefest fashion.

In the laboratory, fats and waxes are resolved into their proximate constituents, viz. into fatty acids and glycerol on the one hand, and into fatty acids and alcohols on the other, by saponification with alcoholic potash solution.

The method for preparing the fatty acids from *oils and fats* may be described here in full once for all: 50 grms. are saponified (see p. 103) by boiling with 40 c.c. of a caustic potash solution of the specific gravity 1·4 and 40 c.c. of alcohol in a flask provided with a reflux tube, or (especially in the case of those fats the fatty acids of which are not likely to undergo rapid oxidation on exposure to the air) in a porcelain dish on a water-bath with constant stirring, until the soap becomes pasty. It is preferable to use the flask when solid fats (and readily oxidisable oils, see below) are saponified, as in an open porcelain dish the soaps are apt to occlude neutral fat, which would thereby escape saponification; besides, it is thus possible to recover the alcohol. The soap is then dissolved in 1000 c.c. of water, and the solution boiled in a porcelain dish to evaporate off the adhering alcohol; this can be effected readily by replacing the water as it boils away. Next the soap is decomposed by means of dilute sulphuric acid. When by continued boiling the fatty acids have been obtained as a clear oily layer, free from solid particles floating on the aqueous liquid, the latter is drawn off by means of a syphon, and the fatty acids are washed several times with hot distilled water until all mineral acid has been removed. Since fatty acids of low molecular weight are soluble in hot water, and may redden litmus paper, methylorange should be used

(p. 124) to test for acidity. The dish containing the fatty acids is then placed on a water-bath, and warmed until the fatty acids are completely liquefied. The water and impurities will settle out, and the warm acids are then poured through a dry plaited filter fitted in a hot-water funnel. The fatty acids thus obtained are sufficiently dry for examination. If the fatty acids solidify at the ordinary temperature, it is advisable to allow the fatty layer to solidify, then to perforate the cake by means of a glass rod, pour off the acid liquid, and wash with hot water as before (cp. also Chap. VIII. "Solidifying Point," "Titer Test").

In order to avoid oxidation of the fatty acids contained in vegetable drying and marine animal oils by exposure to the air, the saponification is best carried out in a flask. The removal of the alcohol and washing is carried out in the flask itself, preferably in an atmosphere of carbon dioxide or hydrogen. For this purpose the flask in which the saponification has been carried out is provided with a cork perforated with three holes, through one of which enters the indifferent gas (carbon dioxide or hydrogen); through the second the gas and vapours pass away, whilst the third is fitted with a syphon which is put in operation whenever wash water has to be drawn off. Thus it is possible to prevent the oxidation of the fatty acids. This is especially necessary in case the further examination of fatty acids for iodine value or for the proportion of unsaturated fatty acids is required. The filtration may also be carried out in an atmosphere of an indifferent gas.

It will be observed that in any case the bulk of the volatile soluble fatty acids are removed with the wash waters. Thus the method of preparing the fatty acids refers essentially to the preparation of the insoluble fatty acids. The soluble volatile fatty acids must be determined separately, according to the methods explained in Chap. VIII.

In order to test for the presence of unsaponified fat, 3 c.c. are dissolved in 15 c.c. of 95 per cent (by volume) alcohol, and 15 c.c. of aqueous ammonia are added. If an appreciable amount of fat has escaped saponification, the mixture will become turbid (*Geitel*). It should, of course, be remembered that, if the sample contain considerable quantities of unsaponifiable matter, turbidity will set in on that account alone.

The acid water and wash waters contain all the glycerol obtainable from the glycerides.

If a *wax* be saponified in the same manner, it should be noted that the fatty layer, obtained as described above, contains both the fatty acids and the alcohols, and also such amounts of hydrocarbons as naturally occur in the wax, whereas the wash waters contain no glycerol.[1] In order to obtain the free fatty acids themselves, recourse must be had to special methods which will be described in Chapter VI.

The mixed fatty acids, or in the case of waxes the mixed acids and alcohols, are then resolved into the individual constituents by scientific methods which will be detailed later on.

[1] Cp., however, "Sperm Oil" and "Arctic Sperm Oil," Vol. II. Chap. XIV.

In the above described manner the acids and alcohols enumerated in the following lists have been isolated from fats and waxes. Those acids and alcohols which have been found hitherto exclusively in waxes are marked (W.), and those which occur in fats as well as in waxes are marked (F.W.); all other acids and alcohols have hitherto been found in oils and in fats only.

A. Acids

I. Acids of the series $C_nH_{2n}O_2$. Acids of the Acetic Series.[1]

$C_2H_4O_2$	Acetic acid
$C_4H_8O_2$	Butyric acid
$C_5H_{10}O_2$	Valeric acid (?)
$C_6H_{12}O_2$	Caproic acid
$C_8H_{16}O_2$	Caprylic acid
$C_{10}H_{20}O_2$	Capric acid
$C_{12}H_{24}O_2$	Lauric acid
$C_{13}H_{26}O_2$	Ficocerylic acid (?) (W.)
$C_{14}H_{28}O_2$	Myristic acid (F.W.)
$C_{15}H_{30}O_2$	Isocetic acid (?)
$C_{16}H_{32}O_2$	Palmitic acid (F.W.)
$C_{17}H_{34}O_2$	Daturic acid
$C_{18}H_{36}O_2$	Stearic acid (F.W.)
$C_{20}H_{40}O_2$	Arachidic acid
$C_{22}H_{44}O_2$	Behenic acid
$C_{24}H_{48}O_2$	Lignoceric acid
$C_{24}H_{48}O_2$	Carnaübic acid (?) (W.)
$C_{24}H_{48}O_2$	Pisangcerylic acid (W.)
$C_{26}H_{52}O_2$	Cerotic acid (W.)
$C_{28}H_{56}O_2$	Montanic acid (W.)
$C_{30}H_{60}O_2$	Melissic acid (W.)
$C_{33}H_{66}O_2$	Psyllostearylic acid (?) (W.)

II. Acids of the series $C_nH_{2n-2}O_2$. Acids of the Acrylic or Oleic Series.

$C_5H_8O_2$	Tiglic acid
$C_{12}H_{22}O_2$	not named
$C_{14}H_{26}O_2$	not named
$C_{16}H_{30}O_2$	Hypogæic acid
$C_{16}H_{30}O_2$	Physetoleic acid (F.W.)
$C_{16}H_{30}O_2$	Palmitoleic acid
$C_{16}H_{30}O_2$	Lycopodic acid[2]
$C_{18}H_{34}O_2$	Oleic acid
$C_{18}H_{34}O_2$	Elaïdic acid
$C_{18}H_{34}O_2$	Isoöleic acid
$C_{18}H_{34}O_2$	Rapic acid
$C_{18}H_{34}O_2$	Petroselinic acid
$C_{18}H_{34}O_2$	Cheiranthic acid
$C_{18}H_{34}O_2$	Liver oleic acid
$C_{19}H_{36}O_2$	Doeglic acid (?)
*$C_{19}H_{36}O_2$	Jecoleic acid
$C_{20}H_{38}O_2$	Gadoleic acid
$C_{22}H_{42}O_2$	Erucic acid
$C_{22}H_{42}O_2$	Brassidic acid
$C_{22}H_{42}O_2$	Isoerucic acid

III. Acids of the series $C_nH_{2n-4}O_2$.

(*a*) Open Chain Acids.

(*α*) Acids of the Linolic Series.

$C_{18}H_{32}O_2$	Linolic acid
$C_{18}H_{32}O_2$	Millet oil acid
$C_{18}H_{32}O_2$	Telfairic acid
$C_{18}H_{32}O_2$	Elæomargaric (Elæostearic) acid

(*β*) Acids of the Tariric Series.

$C_{18}H_{32}O_2$	Tariric acid

(*b*) Cyclic Acids. Acids of the Chaulmoogric Series.

$C_{16}H_{28}O_2$	Hydnocarpic acid
$C_{18}H_{32}O_2$	Chaulmoogric acid

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[1] Hyænic acid, described in the earlier literature of oils and fats as having the formula $C_{25}H_{50}O_2$, has been omitted here; most probably it represented a mixture of several acids.

[2] Aldepalmitic acid, $C_{16}H_{30}O_2$ (Wanklyn, *Journ. Soc. Chem. Ind.*, 1891, 212), has not been admitted to the above list.

* The existence of the acids marked with an * has been inferred from derivatives of such hypothetical acids.

IV. Acids of the series $C_nH_{2n-6}O_2$. Acids of the Linolenic Series.

$C_{18}H_{30}O_2$ Linolenic acid
$C_{18}H_{30}O_2$ Isolinolenic acid

*$C_{18}H_{30}O_2$ Jecoric acid

V. Acids of the series $C_nH_{2n-8}O_2$. Acids of the Clupanodonic Series.

$C_{14}H_{20}O_2$ Isanic acid
*$C_{17}H_{26}O_2$ Therapic acid (?)

$C_{18}H_{28}O_2$ Clupanodonic acid
$C_{20}H_{32}O_2$ Arachidonic acid

VI. Acids of the series $C_nH_{2n}O_3$. Hydroxylated Acids.

$C_{12}H_{24}O_3$ Sabinic acid[1]
$C_{16}H_{32}O_3$ Juniperic acid[1]
$C_{16}H_{32}O_3$ Lanopalmic acid (W.)

$C_{21}H_{42}O_3$ not named
$C_{31}H_{62}O_3$ Cocceric acid (W.)

VII. Acids of the series $C_nH_{2n-2}O_3$. Acid of the Ricinoleic Series.

$C_{18}H_{34}O_3$ Ricinoleic acid
$C_{18}H_{34}O_3$ Isoricinoleic acid
$C_{18}H_{34}O_3$ Ricinelaïdic acid

$C_{18}H_{34}O_3$ Ricinic acid
$C_{18}H_{34}O_3$ Quince oil acid

VIII. Acids of the series $C_nH_{2n}O_4$. Dihydroxylated Acids.

$C_{18}H_{36}O_4$ Dihydroxystearic acid

$C_{30}H_{60}O_4$ Lanoceric acid (W.)

IX. Acids of the series $C_nH_{2n-2}O_4$. Dibasic Acids.

$C_{19}H_{36}O_4$ Heptadecamethylenedicarboxylic acid

$C_{20}H_{38}O_4$ Octodecamethylenedicarboxylic acid
$C_{21}H_{40}O_4$ Japanic acid

B. Alcohols

I. Alcohols of the series $C_nH_{2n+2}O$. Alcohols of the Ethane Series.

$C_{13}H_{28}O$ Pisangceryl alcohol (W.)
$C_{16}H_{34}O$ Cetyl alcohol (Ethal) (W).
$C_{18}H_{38}O$ Octodecyl alcohol (W.)
$C_{20}H_{42}O$ Arachyl alcohol
$C_{20}H_{42}O$ Raphia alcohol (W.)
$C_{24}H_{50}O$ Carnaübyl alcohol (?) (W.)

$C_{24}H_{50}O$ or $C_{25}H_{52}O$ not named
$C_{26}H_{54}O$ Ceryl alcohol (F.W.)
$C_{27}H_{56}O$ Isoceryl alcohol (W.)
$C_{30}H_{62}O$ Melissyl (Myricyl) alcohol (F.W.)
$C_{33}H_{68}O$ Psyllostearyl alcohol (W.)

II. Alcohols of the series $C_nH_{2n}O$. Alcohols of the Allylic Series.

$C_{12}H_{24}O$ Lanolin alcohol (W.)

$C_{15}H_{30}O$ not named

III. Alcohols of the series $C_nH_{2n-6}O$.

$C_{17}H_{28}O$ Ficoceryl alcohol (W.)

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* The existence of the acids marked with an * has been inferred from derivatives of such hypothetical acids.

[1] These hydroxylated acids are stated to occur in the "Etholides" of the *Coniferæ*. See Chap. II. p. 68.

IV. Alcohols of the series $C_nH_{2n+2}O_2$. Alcohols of the Glycolic Series.

$C_{25}H_{52}O_2$ not named

$C_{30}H_{62}O_2$ Cocceryl alcohol (W.)

V. Alcohols of the series $C_nH_{2n+2}O_3$.

$C_3H_8O_3$ Glycerol

VI. Alcohols of the Cyclic Series. Sterols.

(*a*) Zoosterols.

$C_{27}H_{46}O$ Cholesterol (F.W.)
$C_{27}H_{46}O$ Isocholesterol (W.)

$C_{27}H_{46}O$ Bombicesterol
$C_{27}H_{46}O$ Clionasterol

(*b*) Phytosterols.

$C_{27}H_{46}O$ Sitosterol (F.W.)
$C_{28}H_{46}O$ Brassicasterol

$C_{30}H_{48}O$ Stigmasterol
$C_{25}H_{44}O$ Coprosterol

A. ACIDS

Occurrence of Fatty Acids

The fatty acids above enumerated are by no means equally distributed in natural oils, fats, and waxes. Those fatty acids which contain an uneven number of carbon atoms (valeric, ficocerylic, isocetic (?), tiglic acid, etc.) are of comparatively rare occurrence, and are mostly confined to some single individual. Indeed, some of those enumerated will not, perhaps, bear the light of modern investigation with its improved methods of research, and may have to share the fate of medullic,[1] moringic, theobromic,[2] crotonoleic,[3] and umbellulic[4] acids, which must be considered as definitely removed from the list of fatty acids. The fatty acids of the vast majority of oils and fats contain an even number of carbon atoms, and it would almost appear that acids having an uneven number of carbon atoms should on that account alone be looked upon as most likely not belonging to this section. On the strength of this rule the author ventured the opinion that statements as to the occurrence of formic acid in oils and fats should be regarded with suspicion. Most of the acids having an uneven number of carbon atoms have been marked with a (?) in the list.

Recently, however, the identity of an acid occurring in datura oil and having the composition $C_{17}H_{34}O_2$ has been proved by *H. Meyer and R. Beer*, so that the occurrence of at least one higher acid with an uneven number of carbon atoms must be considered as established.

In the brief enumeration of pure glycerides and pure waxes given in Chap. I. the most important fatty acids are given implicitly. Full indications as to their occurrence, as also of the alcohols mentioned in the list, will be found on the following pages of this chapter.

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[1] *Berichte*, 23. Ref. 493.

[2] *Ibid.* 16. 1103.

[3] *Journ. Soc. Chem. Ind.*, 1895, 985.

[4] *Amer. Chem. Journ.*, 1902, 327.

It would also appear that all saturated fatty acids have a normal structure; this induced the author to deviate from the statement found in text-books on "Organic Chemistry," that isovaleric and isobutylacetic acids occur in dolphin oil and butter fat respectively; the acids are described here as valeric and caproic acids.

The existence of the higher fatty acids was practically unknown until *Chevreul* commenced his researches, although, already in 1741, *Claude Joseph Geoffrey* (*Geoffrey the younger*) had observed that on decomposing soap with a mineral acid a fatty substance was obtained, which differed from all known oils and fats by its ready solubility in alcohol. Three years later *Macquer* found that the greater solubility in alcohol of rancid fats and oils as compared with fresh fats and oils is due to the presence of an acid substance. *Fourcroy*, as *Scheele* before him, had found that the fatty matter separated from lead plaster by means of acid differs from the original fat by its greater solubility in alcohol and its greater power to combine with lead hydroxide.

PROPERTIES OF FATTY ACIDS

Specific Gravity

The specific gravities of the fatty acids at different temperatures will be found under the headings of the individual acids.[1] The following table, affording a rapid survey, indicates that the specific gravity decreases with the increase of the number of carbon atoms in the molecule, and that the specific gravities of the unsaturated acids are higher than those of saturated acids having the same number of carbon atoms :—

Acid.	Specific Gravity.	
Acetic	1·0515 at 15° C.	
Butyric	0·9580 „ 14 „	
Valeric	0·9310 „ 20 „	
Caproic	0·9274 „ 20 „	
Caprylic	0·9100 „ 20 „	
Capric	0·8858 „ 40 „	
Lauric	0·875 „ 43·6 „	
Myristic	0·8622 „ 53·8 „	
Palmitic	0·8527 „ 62 „	
Stearic	0·8454 „ 69·2 „	
Cerotic	0·8359 „ 79 „	
Oleic	0·8540 „ 78·4 „	
Elaïdic	0·8505 „ 79·4 „	
Petroselinic	0·8681 „ 40 „	
Erucic	0·8602 „ 55·4 „	
Linolic	0·9026 „ 18 „	(water at 4° C. = 1)
Linolenic	0·9141 „ 18 „	(„ „)

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[1] For speculative views on the Specific Gravities at the Melting Point in Relation to Constitution cp. J. C. Earl, *Chem. News*, 1910, 265.

Solidifying and Melting[1] Points

The lower members of the acetic acid series, up to and including caprylic acid, and further oleic, rapic, doeglic (?), linolic, linolenic, clupanodonic, and ricinoleic acids are liquid at the ordinary temperature. The following table contains the solidifying and melting points of the acids arranged in a synoptical manner :—

Acid.	Solidifying Point. °C.	Melting Point. °C.
Acetic	+17·5	...
Butyric	−19	−6·5
Valeric	−57	−51
Caproic	−8	...
Caprylic	12	16·5
Capric	...	31·3
Lauric	...	43·6
Myristic	...	53·8
Palmitic	62·6	62·62
Daturic	59·5-60	...
Stearic	69·3	69·32
Arachidic	79-77	77·0
Behenic	...	83-84
Lignoceric	...	80·5
Carnaübic	69-67	74
Pisangcerylic	...	72
Cerotic	...	77·8
Montanic	...	83
Melissic	...	91 ; 88·5
Psyllostearylic	...	94-95
Tiglic	...	64·5
Hypogæic	...	33·0
(Gaïdic)	...	(39)
Physetoleic	...	30·0
Oleic	...	6·5 ; 14[2]
(Isoöleic)	...	(44-45)
(Elaïdic)	...	(44·5)
Erucic	...	33-34
Petroselinic	27	33-34
Petroselinelaïdic	...	(54)
(Isoerucic)	...	(54-56)
(Brassidic)	...	(65-66)
Elæomargaric (Elæostearic)	...	47-48
Linolic	below −18	...
Tariric	...	50·5
Hydnocarpic	...	59-60
Chaulmoogric	...	68
Isanic	...	41
Lanopalmic	...	87-88
Cocceric	...	92-93
Ricinoleic	6-10	4-5
Ricinelaïdic	...	52-53
Ricinic	...	81
Dihydroxystearic	...	141-143
Lanoceric	103-101	104-105
Japanic	...	117·7

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[1] Cp. Le Chatelier and (Mlle) Cavaignac, *Compt. rend.*, 1913 (156), 589, and above, p. 22.

[2] Cp. p. 179, "Oleic Acid."

The solidifying points of mixed fatty acids are of great importance in the examination of oils, fats, and wax; the solidifying points being more characteristic than the melting points. It is not possible to infer by calculation the solidifying point of a mixture of pure fatty acids from the solidifying points of the individual fatty acids. This is clearly brought out by the numbers given in the following table, as also by the author's[1] observation that a mixture of two parts of pure stearic acid melting at 69·3° C. and one part of "oleic acid" melting at 14° C., melted at 62·5° to 63·5° C., whereas calculation would lead to a melting point of only 50·9° C.

Mixtures of pure fatty acids are apt to form "eutectic" compounds, behaving, as regards melting and solidifying points, like pure chemical substances. Thus, a mixture of 47·5 per cent of stearic and 52·5 per cent of palmitic acids behaves like a chemical individual and cannot be resolved into its components by crystallisation from alcohol. Further instances of such eutectic compounds will be given in the following pages. It may, however, be pointed out here that several acids which were looked upon as individuals were found to be eutectic compounds. This holds good especially of those acids to which an uneven number of carbon atoms in their molecule has been ascribed.

The melting point of a mixture of two fatty acids cannot be calculated from the melting points of the constituents. As a rule, the melting point lies considerably below the calculated one, sometimes even below the melting point of the lowest melting acid. The following tables will illustrate the above-mentioned facts:—

Solidifying Points of Mixtures of Palmitic and Stearic Acids (de Visser)

Palmitic[2] Acid. Per cent.	Stearic[2] Acid. Per cent.	Solidifying Point. °C.	Palmitic Acid. Per cent.	Stearic Acid. Per cent.	Solidifying Point. °C.
100	0	62·618	56	44	56·36
90	10	59·31	55	45	56·38
85	15	57·80	54	46	56·39
80	20	56·53	53	47	56·40
75	25	55·46	52	48	56·40
71	29	54·92	51	49	56·41
70	30	54·85	50	50	56·12
68	32	55·12	49	51	56·44
66	34	55·38	48	52	56·50
64	36	55·62	47	53	56·63
63	37	55·75	46	54	56·85
62	38	55·88	45	55	57·20
61	39	56·00	40	60	58·76
60	40	56·11	30	70	61·73
59	41	56·19	20	80	64·51
58	42	56·25	10	90	67·02
57	43	56·31	0	100	69·32

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[1] *Jahrbuch der Chemie*, 1899, ix. 353.

[2] The palmitic acid was obtained from vegetable tallow of China, and had been recrystallised thirty times; the stearic acid was prepared from Borneo tallow, and had been recrystallised fifty-one times. Cp. *Berichte*, 1905, 4949.

Solidifying Points of Mixtures of Stearic and Oleic Acids (*Fokin*[1])

Oleic Acid. Per cent.	Stearic Acid. Per cent.	Solidifying Point. ° C.	Oleic Acid. Per cent.	Stearic Acid. Per cent.	Solidifying Point. ° C.
90	10	29·5	40	60	59·8
80	20	40·2	30	70	62·3
70	30	47·7	20	80	64·5
60	40	52·9	10	90	66·3
50	50	56·8	..	100	68·0

Melting Points of Mixtures of Lauric Acid with Myristic, or Palmitic, or Stearic Acid (*Heintz*)

Lauric Acid. Per cent.	With Myristic Acid.		With Palmitic Acid.		With Stearic Acid.	
	Per cent.	Melting Point.	Per cent.	Melting Point.	Per cent.	Melting Point.
		° C.		° C.		° C.
100	0	43·6	0	43·6	0	43·6
90	10	41·3	10	41·5	10	41·5
80	20	38·5	20	37·1	20	38·5
70	30	35·1	30	38·3	30	43·4
60	40	36·7	40	40·1	40	50·8
50	50	37·4	50	47·0	50	55·8
40	60	43·0	60	51·2	60	59·0
30	70	46·7	70	54·5	70	62·0
20	80	49·6	80	57·4	80	64·7
10	90	51·8	90	59·8	90	67·0
0	100	53·8	100	62·0	100	69·2

Melting Points of Mixtures of Myristic Acid with Palmitic or Stearic Acid (*Heintz*)

Myristic Acid. Per cent.	Palmitic Acid.		Stearic Acid.	
	Per cent.	Melting Point.	Per cent.	Melting Point.
		° C.		° C.
100	0	53·8	0	53·8
90	10	51·8	10	51·7
80	20	49·5	20	47·8
70	30	46·2	30	48·2
60	40	47·0	40	50·4
50	50	47·8	50	54·5
40	60	51·5	60	59·8
80	70	54·9	70	62·8
20	80	58·0	80	65·0
10	90	60·1	90	67·1
0	100	62·0	100	69·2

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[1] *Journ. Russ. Phys. Chem. Soc.*, 1912 (44), 155.

Melting Points of Mixtures of Daturic and Palmitic Acids (Meyer and Beer[1]*)*

Daturic Acid. Per cent.	Palmitic Acid. Per cent.	Melting Point. °C.
100	0	59·5
90·6	9·4	56·5-57
83·3	16·7	55 -56
73·5	26·5	54·5-55·5
68·5	31·5	54·5-56
62·4	37·6	54·5-56
55·5	44·5	55·5-57·5
50·0	50·0	56 -58·5
41·7	58·3	58 -59·5
31·2	68·8	58·5-60
20·8	79·2	59·5-60·5
11·1	88·9	60 -61·5
0	100	62

Melting Points of Mixtures of Palmitic and Stearic Acids (Heintz[2]*)*

Palmitic Acid. Per cent.	Stearic Acid. Per cent.	Melting Point. °C.
100	0	62·0
90	10	60·1
80	20	57·5
70	30	55·1
67·5	32·5	55·2
60	40	56·3
50	50	56·6
40	60	60·3
30	70	62·9
20	80	65·3
10	90	67·2
0	100	69·2

Tables giving the melting points of mixtures of not completely purified stearic and palmitic acids, and mixtures thereof with oleic acid, will be found in Vol. III. Chap. XV. "Candle Industry."

Melting Points of Mixtures of Palmitic and Cerotic Acids (Lewkowitsch[3]*)*

Palmitic Acid. Per cent.	Cerotic Acid. Per cent.	Melting Point. ° C.
100	0	60·0
90	10	56·0
85	15	56·5
75	25	60·5
60	40	65·5
50	50	68·6
40	60	70·0
0	100	78·5

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[1] *Mitt. k.k. Akad. Wissens.*, 1912 (121), 1.

[2] *Liebig's Annal.* 92, 295.

[3] Unpublished observations.

Melting Points of Mixtures of Stearic and Cerotic Acids (*Lewkowitsch*[1])

Stearic Acid. Per cent.	Cerotic Acid. Per cent.	Melting Point. °C.
100	0	68·2
95	5	66·7
90	10	65·6
85	15	63·3
0	100	78·5

Boiling Points

Only the following among the more frequently occurring fatty acids can be distilled under ordinary pressure without undergoing decomposition :—

Acid.	Boiling Point. °C.
Butyric	162·3
Caproic	202-203
Caprylic	236-237
Capric	268-270

Owing to their comparatively high vapour tension these acids are readily volatilised with water vapours (cp. also Chap. VIII. " Volatile Acids ") on boiling their aqueous solutions ; hence they are also termed *volatile* fatty acids, in contradistinction to the higher fatty acids (palmitic, stearic, oleic, etc.) the vapour tension of which is so low that they are practically not volatilised in a current of steam at 100° C. ; [2] they are therefore termed *non-volatile* acids. Lauric and, to a lesser extent, myristic acids occupy an intermediate position between the two groups. The *non-volatile* acids, when subjected to dry distillation at ordinary pressure, undergo partial decomposition ; amongst the products of the destructive distillation are found hydrocarbons of the ethane series. Under diminished pressure, however, and with the aid of superheated steam, even these fatty acids can be distilled without suffering decomposition (*Chevreul*). In practice, the distillation with superheated steam under ordinary pressure is largely used in the manufacture of higher fatty acids. More recently the two methods have been combined, and the higher fatty acids are distilled on a large scale in a current of superheated steam *in vacuo* (see Vol. III. Chap. XV.). The action of steam is not only a mechanical or purely physical one, as distillation in a current of hydrogen does not preclude the formation of secondary products. Experiments dealing with carbonic acid as a vehicle in the distillation process have not been published.

The following isolated observations will illustrate the statements made above. If lauric acid (boiling at about 295° C.) or myristic acid (boiling at about 318° C.) are distilled with water or steam under ordinary atmospheric pressure, the distillate contains at most 0·2 per cent of these fatty acids. If, however, the steam be superheated so that the temperature of the myristic acid be kept up at 168·5° C., then the distillate contains at 760 mm. pressure 7·7 per cent myristic acid, and at 38 mm. pressure the distillate will contain 65·7 per cent (*C. von Rechenberg*). Further data will be given under the heading of the individual acids described below.

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[1] Unpublished observations.

[2] Cp. Chap. VIII.

The following boiling points have been found at the reduced pressures stated, and *in vacuo* :—

Acid.	Boiling Point at 100 mm. Pressure.	Boiling Point at 15 mm. Pressure. (Krafft and Weilandt.[1])	Boiling Point *in vacuo.* (Krafft and Weilandt.[1])	Boiling Point *in vacuo.* (Caldwell and Hurtley.[2])	Temp. of bath.
	° C.	° C.	° C.	° C.	° C.
Lauric . .	225	176	102	89	100
Myristic .	250·5	196·5	121-122	98	130
Palmitic .	271·5	215	138-139	114	140
Daturic .	227	..	143·6 [7]	..	..
Stearic . .	291	232·5	154·5-155·5	128	160
Hypogæic [3] .	..	236	..	..	..
Oleic . .	285·5-286	232·5	153	130	160
Elaïdic . .	287·8-288	234	154	..	..
Erucic . .	..	264	179	..	..
Brassidic .	..	265	160	..	..
Linolic . .	229-230 [4]	..	..	..	..
Chaulmoogric	..	247-248 [5]	..	..	..
Ricinoleic .	..	250	..	..	..
Ricinic . .	..	250-252	..	..	..
Elæostearic .	..	235 [6]	..	..	..
Linolenic .	..	..	157-158	..	..

The lowest temperatures at which volatilisation of lauric, myristic, palmitic, and stearic acids in a complete vacuum could be ascertained were 22°, 27°, 32°, and 38° C. respectively.[8] The details of the experiments are given in the following table :—

Acid.	Temperature.	Duration of Experiment.	Weight of Substance.	Loss of Weight.
	° C.	Hours.	Grms.	Grms.
Lauric . .	22	6	0·8215	0·0005
	36	4	0·8310	0·0095
Myristic . .	27	6	0·4263	0·0003
	28	10	0·4269	0·0006
Palmitic . .	32	12	0·48402	0·00012
	36	12	0·8359	0·0012
Stearic . .	38	12	0·62663	0·00012
	39	10	0·6982	0·0013

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[1] *Berichte*, 1896, 1324.

[2] *Journ. Chem. Soc.*, 1909, 855.

[3] Bodenstein, *Berichte*, 1894, 3399.

[4] Under 16 mm. pressure ; and 228° C. under 14 mm. pressure.

[5] Under a pressure of 20 mm.

[6] R. Majima, *Berichte*, 1909, 675.

[7] Bömer and Limprich, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (23), 648.

[8] Chz. J. Hansen, *Berichte*, 1909, 210.

Solubility

The lowest members of the acetic series are miscible with water in every proportion.[1] Caproic acid is no longer miscible with water; 100 c.c. of water dissolve 0·882 grm. at 15° C. Caprylic acid requires for its solution 400 parts of boiling water; on cooling, the acid separates out almost completely. At 15° C., 100 c.c. of water dissolve 0·079 grm. of caprylic acid.

The solubility in water decreases rapidly with the increase of the number of carbon atoms in the molecule. Capric acid is practically insoluble in cold water, somewhat more soluble in hot water. Lauric acid is very slightly soluble in boiling water. The higher acids are practically insoluble in water.

Taking the solubility in water as a basis for classification, we may, for analytical purposes, subdivide the fatty acids into *soluble* and *insoluble* fatty acids. The acids up to caprylic acid are termed *soluble* fatty acids; the higher fatty acids from myristic acid upwards are the *insoluble* fatty acids. Capric and lauric acids occupy, also as regards solubility, an intermediate position (cp. Chap. VIII.).

All fatty acids, without exception, are soluble in hot absolute or high strength alcohol; the higher fatty acids, from palmitic upwards, are sparingly soluble in cold alcohol. The highest acids are almost insoluble in cold alcohol. By repeatedly boiling an alcoholic solution of higher fatty acids or boiling down their alcoholic solutions, slight esterification takes place, which may in some cases cause appreciable errors.[2]

In dilute alcohol (below 60 per cent) the higher acids are practically insoluble, cp. Chap. VIII.

The fatty acids are readily soluble in ether, carbon bisulphide, chloroform, and carbon tetrachloride. With the exception of the hydroxylated fatty acids (see Chap. VIII.) the liquid and unsaturated fatty acids dissolve easily in petroleum ether. The solid fatty acids also dissolve readily on warming.

Further data will be found in Chap. V. under "Solubility."

Refractive Index

The magnitude of the refractive index increases with the increase of the number of carbon atoms in the molecule. The unsaturated fatty acids show a higher refraction than the saturated acids containing the same number of carbon atoms. This is shown by the following table; further details will be found under the heading of each individual acid.

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[1] With regard to "eutectic" mixtures of formic, acetic, and propionic acids with water cp. A. Faucon, *Compt. rend.*, 1909 (148), 38; R. Ballö, *Chem. Zentralb.*, 1910, 2073.

[2] Emerson and Dumas, *Journ. Amer. Chem. Soc.*, 1909, 949.

Acid.	Refractive Index.
Butyric	1·39906 at 20° C.
Caproic	1·41635 „ 20 „
Caprylic	1·42825 „ 20 „
Capric	1·42855 „ 40 „
Lauric	1·42665 „ 60 „
Myristic	1·43075 „ 60 „
Palmitic	1·42693 „ 80 „
Margaric	1·4342 „ 60 „
Stearic	1·43003 „ 80 „
Oleic	1·44710 „ 60 „
Petroselinic	1·4533 „ 40 „

Optical Rotation

Hitherto the specific rotations of the following three pure fatty acids have been determined (cp. also Chap. V. " Rotatory Power of the Plane of Polarisation ").

Acid.	Specific Rotation.
Ricinoleic	+ 6·25
Hydnocarpic	+68·1°
Chaulmoogric	+56

For the resolution of racemic dihydroxystearic acid into two optically active isomerides see p. 228. For optically active acids in " Rump Gland Wax " see Vol. II. Chap. XIV.

Viscosity

Since viscosimetric methods have been proposed for the examination of oils and fats, it will be found useful to have a record of the following viscosimetric constants. From the values given in the table, it is evident that the viscosity increases with the molecular weight.[1]

Viscosimetric Constants of Fatty Acids (Pribram and Handl)

Fatty Acid.	Molecular Weight.	Specific Viscosity at		
		10° C.	80° C.	50° C.
Propionic	74	70·3	51·5	49·9
Butyric	88	110·2	77·4	57·6
Valeric	102	152·4	103·3	71·5
Caproic	116	222·2	139·7	97·8

With regard to the following physical constants: specific heat, heat of neutralisation, latent heat of fusion and of solidification, and surface tension, *Guillot's* [2] pamphlet and the paper given in the footnote [3] should be consulted. As to heats of combustion of fatty acids cp. Chap. V.

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[1] Cp. also Tsakalotos, *Compt. rend.*, 1908 (146), 1146.

[2] *Propriétés Physiques de la Série Grasse.* Paris. Ballière et fils, 1895. For the constants of affinity see Tellmann and Schliemann, *Liebig's Annal.* 274, 144; cp. also D. E. Tsakalotos, *Compt. rend.*, 1908 (146), 1146.

[3] G. Massol and A. Faucon, *Compt. rend.*, 1909 (149) 353; 1911 (153), 268.

Salts of Fatty Acids

Fatty acids combine readily with solutions of caustic soda and of caustic potash to form "soaps." In dilute aqueous solution the chemical union does not take place in molecular proportions, so that free fatty acids and free alkali can co-exist to a certain extent (see below, "Hydrolysis of Soaps"). In alcoholic solutions, however, combination takes place in stoichiometric proportions. The carbonates of the alkali metals react with fatty acids in aqueous solution at somewhat elevated temperatures, forming salts of fatty acids with evolution of carbonic acid.[1]

In common parlance, we generally understand under the term "soaps" the alkali salts of the non-volatile fatty acids, whereas the term "metallic salts of the fatty acids," denotes the salts of the heavy metals. I shall consider the salts of the fatty acids under the following two large groups:—(1) Salts of the alkali metals, including ammonia soaps; (2) Salts of the alkaline earths, and of the heavy metals (cp. Vol. III. Chap. XV. "Soap Manufacture").

(1) *Salts of the Alkali Metals, including Ammonia Soaps—Water-Soluble Soaps*

The normal salts of the saturated acids have the general formula $C_nH_{2n+1}CO.OM$, where M stands for Na, or K, or NH_4. They are obtained by the direct union of fatty acids with sodium or potassium hydrate, with elimination of water. They are also formed by heating an aqueous solution of sodium or potassium carbonate with fatty acids, when carbon dioxide is evolved.[2] (From a physiological point of view it is interesting to note that whilst palmitic, stearic, and oleic acids at a temperature of 37° C. (blood temperature) act but very slowly on a dilute solution of sodium carbonate, they form the respective sodium salts much more readily in the presence of bile secretions.) The salts may also be prepared by adding boiling solutions of the carbonate to alcoholic solutions of fatty acids, evaporating to dryness and exhausting the residue with alcohol. The salts deposit from the alcohol on cooling. If pure materials are employed, the salts can thus be obtained in their crystalline state. In alcoholic solution these salts are neutral to phenolphthalein. Besides the neutral salts there exist also acid salts of the formula $C_nH_{2n+1}CO.OM, C_nH_{2n}O_2$; these show in hot alcoholic solutions an acid reaction to phenolphthalein.

Since in commercial analysis the fatty acids are frequently estimated by titration with solutions of alkalis, it is important to consider in some detail the behaviour of fatty acids towards the indicators used in volumetric analysis. From the large number of indicators which have been proposed from time to time, I select for use in the analysis of fats, methylorange and phenolphthalein, which will be found quite sufficient for all purposes. Tincture of litmus (the place of which has lately been taken by lacmoid) still enjoys some popularity, and may be used in conjunction with the above-named two indicators.[1]

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[1] Cp. Lewkowitsch, *Jahrbuch der Chemie*, 1899, ix. 357; Fendler and Kuhn, *Zeits. f. angew. Chem.*, 1909, 107.

[2] The sodium salts are also obtained by allowing fatty acids to act on sodium percarbonate or perborate (Wolffenstein, English patent 16,823, 1908; P. Beirsdorf & Co., French patent 392,955).

Methylorange[2] dissolves in water yielding a yellow liquid, which turns crimson on the addition of a strong acid (appearing yellowish-red in deep layers) owing to the formation of a salt. The change from the yellow of the neutral to the red of the acid solution is especially sharp in very dilute solutions. Weak acids, such as carbonic acid, do not change the colour; therefore, it is possible to use methylorange as an indicator when titrating carbonates, without it being required to drive off the dissolved carbon dioxide by boiling. The acid carbonates of the alkalis are alkaline to methylorange (difference from phenolphthalein). This indicator is specially suitable for the estimation of mineral acids, and offers the further advantage that it can, and indeed must, be used in the cold. Boric acid, however, is not affected by methylorange; even concentrated aqueous solutions of the acid are not reddened.

The soluble fatty acids also redden a solution of methylorange, but on titrating with normal alkali, the end-reaction is not sharp, and the red colour disappears whilst considerable quantities of free fatty acids are still in the solution; therefore methylorange cannot be used for titrating soluble fatty acids, not even acetic acid.[3] Insoluble fatty acids, such as stearic or oleic, do not affect this indicator at all in their alcoholic solutions, nor do they act on it when shaken in the liquid state with an aqueous solution of methylorange.

It is, therefore, feasible, when using methylorange as an indicator, to titrate mineral acids in presence of the higher fatty acids (cp. Vol. III. Chap. XV. "Analysis of Soap"). Methylorange offers the further advantage, that it can be employed in conjunction with phenolphthalein. Thus, in a solution of mineral and higher fatty acids, the mineral acid may be estimated first by using methylorange as an indicator; then after adding phenolphthalein, the higher fatty acids may be titrated.

A convenient solution of the indicator is prepared by dissolving 1 grm. in 1000 c.c. of water. Four drops of this solution are sufficient for every 100 c.c. of the liquid to be titrated.

Phenolphthalein.—This indicator is obtained commercially in sufficient purity. To prepare the solution required for volumetric analysis, 1 grm. is dissolved in 100 c.c. of 95 per cent alcohol. (It is worth noting that phenolphthalein is insoluble in petroleum ether.) Two drops of this indicator will be found sufficient for every 100 c.c. of a solution. The alcoholic solution of phenolphthalein is yellowish.

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[1] With regard to alkali-blue cp. Chap. VI. "Saponification Value."

[2] According to *Lunge*, tropæolin 00 or 000 is often sold as methylorange. I have occasionally met with methylorange having such strong alkaline reaction, that four drops of a $\frac{1}{10}$ per cent solution required 0·1 c.c. of normal acid for neutralisation. Methylorange should, therefore, always be examined before use.

[3] Schidrowitz (*Analyst*, 1903, 234) showed that acetic acid can be titrated with methylorange as an indicator, if alcohol be added to the solution. Cp., however, Richardson and Bowen, *Journ. Soc. Chem. Ind.*, 1906, 836, and Schidrowitz (*Analyst*, 1907, 4).

On adding it to an acid solution no colouration is produced, but a pink colour appears in the presence of the smallest quantity of a fixed alkali, owing to the formation of a salt.[1] This salt is decomposed completely even by weak acids; hence the insoluble fatty acids can be titrated in their alcoholic solutions in presence of this indicator. Ammonia does not give a sensitive colour reaction with phenolphthalein, and hence is unsuitable for the titration of fatty acids. Phenolphthalein may also be used for the titration of the soluble fatty acids in the same way as is litmus. Due regard should be paid to the sensitiveness of phenolphthalein to carbon dioxide, and to the fact that the acid carbonates of the alkalis do not act on phenolphthalein like the carbonates; [2] it is therefore absolutely necessary to remove any carbon dioxide by boiling. When standardising acids and alkalis with the aid of phenolphthalein, this possible source of error should especially be guarded against.

Litmus.—Tincture of litmus may be used in the analysis of fats for the titration of the volatile fatty acids, mineral acids, caustic alkalis, carbonates, etc. The statement made by *Rechenberg*,[3] that the salts formed by the union of volatile fatty acids with alkalis and alkaline earths—especially those of butyric acid—show in their aqueous solution strongly alkaline reaction, has not been confirmed in the author's experience. It is quite possible to titrate butyric acid, using litmus as an indicator. The change is somewhat gradual, but perfectly distinct.

An aqueous solution of caproic acid strongly reddens litmus; a cold solution of caprylic acid reddens it faintly, whilst a hot solution gives a deeper red. A hot solution of capric acid no longer acts on litmus (*Lewkowitsch*).

It may be noted that the indicators do not actually give the end point, but only the equilibrium point of the reaction; but for practical purposes these two points lie near enough each other to enable us to disregard the very slight excess of acid or alkali (as the case may be) used.

The alkali salts of the fatty acids are remarkable in their behaviour to water.

The salts of the lowest members of the series are easily soluble in water. Thus the alkali salts of butyric acid are deliquescent; those of capric acid are still very easily soluble in water at the ordinary temperature. The solubility in water decreases, however, as the molecular weight of the fatty acids increases; thus the alkali salts of palmitic and stearic acids are no longer soluble in cold water. They dissolve, however, if boiled with not too large a quantity of water, to clear solutions, which solidify, on cooling, to mucilaginous masses practically representing the normal salts of the fatty acids.

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[1] It may be noted that concentrated aqueous solutions of alkali give colourless salts of phenolphthalein; on diluting with water, however, the pink colouration appears.

[2] The frequently repeated statement, that sodium bicarbonate does not redden phenolphthalein in aqueous solution, is not quite correct.

[3] *Journ. f. prakt. Chemie*, 1884, 519.

On diluting the clear hot solutions with water they become turbid, and, on shaking, a lather is produced which persists for some time. The turbidity is due to the dissociation of the normal salt into caustic alkali and free fatty acid. This dissociation, termed *hydrolysis of soap*, is a very gradual one, and depends on the amount of water present and also on the temperature.

The free alkali remains in solution, and the free fatty acid combining with non-hydrolysed salt separates as an acid salt,—*i.e.* a salt containing more than one equivalent of acid for one equivalent of alkali—presumably in association with some undissociated salt.

Chevreul, who first studied this property of alkali-metal soaps, found that a solution of one part of neutral potassium stearate, $C_{18}H_{35}O_2.K$, in 20 parts of boiling water, yields, after the addition of 1000 parts of boiling water, on cooling, an acid salt of the composition $C_{18}H_{35}O_2K.C_{18}H_{36}O_2$—*potassium bistearate*—whilst free alkali and an infinitesimal quantity of stearic acid remain in solution. Similarly, neutral sodium stearate dissolved in 2000 to 3000 parts of boiling water yields, on cooling, an acid salt of the composition $C_{18}H_{35}O_2Na.C_{18}H_{36}O_2$—*sodium bistearate.* Neutral oleate, however, requires a very large quantity of water and a low temperature in order to become dissociated; the difference between oleic acid on the one hand, and palmitic and stearic acids on the other hand, is so marked that an approximate method of separation may be based on this property.

The potassium bistearate described above can be dissociated by further treatment with water into a more acid salt, presumably of the composition of a quadro-stearate.

The amount of alkali thus set free under given conditions can be determined quantitatively by throwing up the soap by common salt (salting out the "curd"), filtering off, washing with brine, dissolving the curd in absolute alcohol, and determining the acidity by titration with alkali, using phenolphthalein as an indicator.

Alder Wright and Thompson[1] derived from a series of observations the results contained in the following table. I have arranged the fatty acids in the order of their molecular weights :—

Fatty Acids.	Mean Molecular Weight.	Hydrolysis brought about by x Molecules of Water.				
		$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Crude lauric . .	195	3·76	4·5	5·4	6·45	7·1
(Cotton seed oil acids .	250 [2]	2·25	3·0	5·0	7·5	9·5)
Nearly pure palmitic .	256	1·45	1·9	2·6	3·15	3·75
(Palm-oil-tallow acids	271	1·1	1·55	2·6	4·1	5·3)
Pure oleic . . .	282	1·85	2·61	3·8	5·2	6·65
Pure stearic . .	284	0·7	1·0	1·7	2·6	3·55

The numbers represent the quantities of Na_2O set free by hydrolysis, calculated for 100 parts of Na_2O contained in the soap in combination with fatty acid, *x* molecules of water being used for one of anhydrous soap.

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[1] *Journ. Soc. Chem. Ind.*, 1885, 630.

[2] This value is too low.

If we look at the numbers given for lauric, palmitic, and stearic acids only, it would appear that the sodium salts of the fatty acids are decomposed with greater ease, the *lower* their molecular weight. But on the one hand the behaviour of oleic acid does not conform to this rule, and on the other hand *Thomsen* [1] has shown that sodium acetate is not sensibly dissociated by water. (Cp., however, p. 132.)

Rotondi [2] explained the action of water on soap in the following manner: Neutral (commercial) soaps, on being dissolved in water, are decomposed into basic and acid salts; the latter are insoluble in cold, and only slightly soluble in hot water. The acid salts not being dialysable, can therefore be separated from the basic salts which readily pass through membranes. The basic soaps are readily soluble in cold and hot water, and are completely precipitated by sodium chloride without loss of alkali; their solutions dissolve acid soaps on heating, but become turbid on cooling.

Rotondi's views have been shown to be erroneous by *Krafft and Stern* [3] who, on repeating *Chevreul's* experiment with pure sodium palmitate (2 grms.), obtained the following result: [4]—

1 Part of Sodium Palmitate containing 8·27 per cent of Na:	
Boiled with parts of Water:	Yielded, on cooling, salt containing Na
	Per cent.
200	7·01
300	6·84
400	6·60
450	6·32
500	6·04
900	4·20

In order to furnish an insight into the approximate composition of the separated salts, the following table is given:—

Salts of the formula	Contain Na. Per cent.
$C_{16}H_{31}O_2Na$	8·27
$3C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$	6·33
$C_{16}H_{31}O_2Na + C_{16}H_{32}O_2$	4·31
$C_{10}H_{31}O_2Na + 3C_{16}H_{32}O_2$	2·20

Similar experiments with pure sodium stearate gave the following result:—

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[1] *Thermochemische Untersuchungen*, i. 372.

[2] *Journ. Soc. Chem. Ind.*, 1885, 601.

[3] *Berichte*, 1894, 1747.

[4] According to Smits (*Zeits. f. physik. Chem.*, 1903, 608) a normal (aqueous) solution of sodium palmitate does not show signs of hydrolysis.

1 Part of Sodium Stearate containing 7·52 per cent of Na:		
Boiled with parts of Water:	Yielded, on cooling, salt containing Na	
	Per cent.	
	I.	II.
200	6·34	6·27
300	5·81	5·71

Sodium bistearate, $C_{18}H_{35}O_2Na + C_{18}H_{36}O_2$, contains 3·89 per cent of Na.

From these experiments the conclusion must be drawn that hydrolysis increases with the molecular weight of the fatty acids; this is in direct opposition to the conclusions derived from *Alder Wright and Thompson's* more complete series of observations detailed above (p. 126).

As shown already, oleic acid occupies an exceptional position as regards the hydrolysis of its salts. This has been confirmed by *Krafft and Stern*, who observed that pure neutral sodium oleate dissolves in about 10 parts of *cold* water to a *clear* solution, which does not become sensibly turbid even after dilution with 900 parts of water, whereas sodium bioleate, $C_{18}H_{33}O_2Na + C_{18}H_{34}O_2$, is immediately dissociated by cold water. In order to hydrolyse oleates, much larger quantities of water are required; at the same time the temperature must be lowered considerably.

The solid elaïdic acid, however, simulates stearic acid in its behaviour, as the following observations prove:—

1 Part of Sodium Elaidate containing 7·56 per cent of Na:	
Boiled with parts of Water:	Yielded, on cooling, salt containing Na
	Per cent.
300	5·80
1500	3·24

In the light of these experiments, those commercial soaps, which consist chiefly of palmitate, stearate, and oleate, would yield, on treatment with large quantities of water, acid palmitate and stearate as precipitates, whereas free alkali and oleate remain in solution. The solution would thus contain soap *plus* free alkali, a fact which has been taken by *Rotondi* as a proof for the existence of basic soaps in solution. Moreover, direct experiments made with a view to preparing synthetically basic salts from oleic acid failed completely, and on hydrolysing pure sodium palmitate with 900 parts of water, not a trace of palmitic acid could be detected in the cold supernatant solution.

The direct proof for the fact that free fatty acid and free alkali co-exist in a dilute solution in the hot was given by extracting a solution of not completely hydrolysed normal sodium palmitate with toluene, when free palmitic acid was obtained.

The hydrolysis of soaps becomes complete, according to *Krafft and*

Wiglow,[1] if the one of the two components of the normal salt—for instance, the fatty acid—is removed (by shaking out repeatedly with toluene).

This statement, however, is not consistent with the fact detailed below, namely, that free alkali prevents hydrolysis. Theoretically, it must, therefore, be expected that in a soap solution an equilibrium would be established between the hydrolysing tendency of water and the opposite tendency of free alkali to prevent hydrolysis. Hence it would follow that if a certain amount of water be added to a soap solution, a definite quantity only, but not the whole quantity of fatty acid, can be extracted, and that a certain amount of soap must remain undissociated in the solution, such soap being protected, as it were, from further hydrolysis by the amount of alkali set free in consequence of the hydrolytic dissociation that had taken place so far. In order to verify this view by experiment,[2] I prepared anhydrous soaps from pure palmitic acid, pure stearic acid, and commercial oleic acid (containing about 8 per cent of solid acids). Two series of experiments were made with one gram of each anhydrous soap; in the one series the soaps were dissolved in 400 c.c. of water, and in the second series in 900 c.c. of water. The soap solutions were boiled under a reflux condenser, and then shaken out with toluene. The boiling and shaking out was repeated eight times; the toluene was then evaporated and the free fatty acids recovered from it and weighed. The alkali in the soap solutions was determined by titration in three stages; the solutions were first titrated in the cold, using phenolphthalein as an indicator. They were then boiled, and titrated after boiling, again using phenolphthalein as an indicator. Finally the solutions were titrated with methylorange as an indicator. The amounts of alkali so found are set out in the following table. The fatty acids recovered from the toluene solutions were weighed and calculated to anhydrides; the numbers are given in the following table. The theoretical amounts of alkali and anhydrides are added for comparison.

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[1] *Journ. Soc. Chem. Ind.*, 1896, 206.

[2] Cp. *ibid.*, 1907, 590.

[TABLE

Hydrolysis, by means of Water, of 1 grm. of pure Anhydrous Soap (Lewkowitsch)

Na_2O.	From					
	Oleic Acid (commercial).		Stearic Acid.		Palmitic Acid.	
	400 c.c. water. Per cent.	900 c.c. water. Per cent.	400 c.c. water. Per cent.	900 c.c. water. Per cent.	400 c.c. water. Per cent.	900 c.c. water Per cent.
By phenolphthalein, in the cold .	3·93	2·87	7·83	4·32	5·96	4·13
,, ,, after boiling .	3·25	5·9	0·23	3·76	5·19	7·03
By methylorange	3·18	1·38	2·2	2·93	0·60	0·61
Total Na_2O, found . . .	10·36	10·15	10·26	11·01	11·75	11·77
Theory . . .	10·197		10·03		11·15	
Fatty Anhydrides—						
Hydrolysed	77·369	75·59	85·47	85·014	81·29	82·97
Not hydrolysed	9·37	5·25	2·71	3·3	1·94	1·96
Insoluble in water and ether .	0·17	0·84	1·43	0·18	1·5	0·29
Total found	86·709	81·68	89·61	88·494	84·73	85·22
Theory . . .	89·803		89·87		88·85	

It will be seen from the above experiments that the quantity of soda found is slightly greater than theory requires; this can easily be explained by the action of the water on the glass vessels. The amount of fatty anhydrides found in the case of oleic acid is much below theory; this must be due to oxidation that had taken place on drying the oleic acid. Although in the other two cases also the agreement between experiment and theory is not so satisfactory as might be expected (owing to the large quantity of solvent used, and the large number of operations through which the small quantity of fatty acids had to be put), still the experiments fully bear out the theoretical postulate that complete hydrolysis is impossible. In the case of palmitic acid the hydrolysis had reached a remarkably high degree; this would readily explain the statements of *Krafft and Wiglow*, who worked especially with palmitic acid.

From the foregoing notes it is apparent that oleic acid behaves differently from the solid fatty acids and even from elaïdic acid, with which it is isomeric. This difference, however, disappears if not only the one factor, which has been considered hitherto exclusively, viz. the proportion of water, be taken into account, but if due regard be had to the temperature. For *Krafft and Wiglow* [1] observed that the temperature at which the separation of acid salts commences always lies below the melting point of the corresponding fatty acid. I have compiled the following table from the earlier experiments of *Krafft and Wiglow*, in which a 1 per cent aqueous solution of the sodium salt was examined, and from some later experiments published by *Krafft*.[2]

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[1] *Journ. Soc. Chem. Ind.*, 1896, 206.

[2] *Berichte*, 1899, 1598.

I have also corrected the melting points of the free acids where necessary.

Sodium Salt of	I. Temperatures of Separation from Aqueous Solutions, containing per cent:				II. Temperature of Separation from 1 per cent Solution.	III. Melting Point of Acid.	IV. Difference, III.-II.	V. Melting Points of the Dry Salts.
	25	20	15	10				
	° C.	° C.	° C.	° C.	° C.	° C		° C.
Stearic acid	...	69	68	63-67	60	69·2	9·2	about 260
Palmitic ,,	...	62-61·8	...	...	45	62·0	17·0	,, 270
Myristic ,,	...	53-52	...	...	31·5	53·8	22·3	,, 250
Lauric ,,	45-42	about 36	...	...	11	43·6	32·6	255-260
Elaïdic ,,	...	45·5-44·8	...	...	35	44·0	9·0	225-227
Oleic ,,	13·6	...	...	...	0	14·0	14·0	232-235
Erucic ,,	...	35-34	...	...	27	33·5	6·5	230-235
Brassidic ,,	...	56	...	...	42	65·5	23·5	245-248

From these numbers the following rule has been derived by *Krafft*: The temperatures of crystallisation of soaps always lie below the melting points of their free fatty acids, and the difference between the two temperatures increases as we descend in the homologous series.[1]

It will thus be seen that oleic acid falls in line with the other acids, and that, *e.g.*, a hot solution of sodium palmitate behaves like a cold solution of sodium oleate.

In dilute solutions the sodium salts of the higher fatty acids would therefore behave like crystalloids (cp. Vol. III. Chap. XV. "Soap Manufacture").

A. Reychler,[2] who repeated *Krafft's* experiments, finds, however, that the temperature at which crystallisation of dilute sodium palmitate solution begins, becomes progressively higher with increasing concentration. It is especially remarkable that the separation of crystals takes place almost completely within a small interval of temperature, so that the filtrate from the crystals obtained a few degrees below the temperature of crystallisation, does not yield an appreciable quantity of salt. Solutions of sodium palmitate of a concentration of $\frac{1}{20}$ and $\frac{1}{40}$ normality are clear in the hot and yield the first acicular crystals between 47°-45° C., and then crystallise completely in lengthy laminæ at 43°-42° C. *They thus form the seat of a distinct crystallisation in a clear medium.* A $\frac{1}{50}$ normal solution becomes slightly cloudy at 45° C., and acicular crystals form at 42·5° C. A ready separation of the crystals takes place at about 40·5° C. Solutions between $\frac{1}{50}$ and $\frac{1}{250}$ normality are more or less opalescent at a high temperature and become iridescent a little below 50° C. At 40°-36° C. a somewhat rapid separation of extremely fine crystals, not recognisable as such with the naked eye, takes place. Thus indistinct crystallisation in a turbid medium is observed. Solutions of $\frac{1}{400}$ normality are both opalescent and iridescent, and crystalline granules only separate out. On raising the temperature of the solutions after their crystallisation any iridescence present disappears at temperatures slightly above 50° C.

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[1] Observations of "temperatures of crystallisation" of concentrated solutions of the sodium salts of lauric, myristic, palmitic, stearic, oleic, elaïdic, erucic, and brassidic acids are recorded by L. Hoeren, *Inaug. Dissert.*, Heidelberg, 1898. The application of the principle underlying the above given observations to the resolution of practical problems has been proposed by Tortelli and Fortini, *Chem. Zeit.*, 1910, 890. Cp. Chap. XII.

[2] *Bull. Soc. Chim. Belg.* (Jubilee Number), 1912, 194. Cp. A. Reychler, "Contributions à l'Étude des Savons," read before the Eighth International Congress.

The sodium palmitate used for these experiments had, as the author calculates from the data given by *Reychler*, the following composition :—

	Per cent.
Sodium palmitate	98·63
Free palmitic acid	0·31
Water	1·06

The electrical conductivities of the above solutions correspond to the phenomena of crystallisation (see below).

From a series of observations carried out by *Krafft and Wiglow* [1] with a view to determining the molecular weight of soaps by the ebullioscopic method, it appears that the sodium salts of the lower fatty acids raise the boiling point of water by twice the normal value; this is explained by the assumption that each molecule is hydrolysed into free fatty acid and sodium hydroxide, as is indicated by the following equation :—

$$\underset{\text{Sodium Acetate}}{C_2H_3O_2Na} + H_2O = \underset{\text{Acetic Acid}}{C_2H_4O_2} + NaOH.$$

The sodium salts of the higher fatty acids do not raise the boiling point of water; the solutions solidify on cooling to gelatinous masses, and thus show the characteristic behaviour of colloids (cp. Vol. III. Chap. XV. "Soap Manufacture").

The observations of *Krafft and Wiglow* are reproduced in the following table :—

Sodium Salts of Acid.	Formula.	Parts of Salt in 100 parts of Water.	Molecular Weight.		$\frac{\text{Apparent Mol. W.}}{\text{Normal Mol. W.}}$
			Apparent.	Normal.	
Acetic .	$C_2H_3O_2Na$	0·9 25·2	50·5 40·3	82	0·6 0·5
Propionic .	$C_3H_5O_2Na$	3·8 19·8	51·7 46·2	96	0·6 0·5
Caproic .	$C_6H_{11}O_2Na$	3·5 20·6	72·8 77·9	138	0·52 0·56
(Nonylic .	$C_9H_{17}O_2Na$	3·4 20·4	144·1 285·5	180	0·8 1·58)
Lauric .	$C_{12}H_{23}O_2Na$	3·3 16·1	474 507	222	2·13 2·28
Palmitic .	$C_{16}H_{31}O_2Na$	16·4 25·0	about 1060 approaching ∞	278	about 4 approaching ∞
Stearic .	$C_{18}H_{35}O_2Na$	abt. 16·0 27	about 1500 approaching ∞	306	about 5 approaching ∞
Oleic .	$C_{18}H_{33}O_2Na$	26·5	approaching ∞	304	approaching ∞

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[1] *Berichte*, 1896, 1329.

The numbers given in the last column are, in the opinion of *Krafft and Wiglow*, a measure of the dissociation brought about, and would thus show in a general way that the salts of the lowest fatty acids are hydrolysed in the hot, those of the higher acids even in the cold, whereas laurates occupy an intermediate position.[1]

In the case of acetic acid at least, it is certainly very difficult to agree with the views of *Krafft and Wiglow*, as acetic acid can be determined quantitatively by titration with alkali in aqueous solutions.[2] In the case of the higher fatty acids, which can no longer be titrated with quantitative results in aqueous solutions, their opinions become more acceptable, especially so in consideration of the experiments described above.

The hydrolysis of sodium stearate might then be represented in the following manner—

$$C_{18}H_{35}O_2.Na+H_2O \rightleftharpoons C_{18}H_{35}O_2.H+NaOH,$$

expressing the fact that an equilibrium is established between free stearic acid, free caustic soda, and sodium stearate.

As regards the values given in the last column for the first three acids, which show that the molecular weights are apparently only half the theoretical ones, the modern ionisation theory seems to afford the better explanation, namely, that the salts are broken up into two ions, the sodium ion and the fatty acid ion.[3]

J. W. M'Bain and M. Taylor[4] derived from a study of the electrical conductivities of solutions of sodium palmitate the conclusion that—in contradistinction to the observation of *Krafft and Wiglow*—normal soaps in concentrated aqueous solutions are not colloids. The ebullioscopic method employed by *Krafft and Wiglow* is considered to be faulty in its application to sodium palmitate solutions on account of the influence which air occluded in, or absorbed by, the viscous soap solutions has on the measurements. A better insight into the nature of sodium palmitate solutions is obtained, according to *M'Bain and Taylor*,[5] by studying the electrical conductivities of sodium palmitate solutions of 0·01-1·5 normality. These observers arrive at the conclusion that normal soaps, even in their most concentrated solutions, are not colloids but mixtures of colloidal acid sodium palmitate, formed hydrolytically, free sodium hydrate, and probably electrolytically dissociated neutral palmitate. *Reychler*, however, concludes from his above-stated observations, that soap solutions, especially those which are neither too dilute nor too hot, represent colloidal media.[1]

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[1] The amines of fatty acids represent similar phenomena inasmuch as lower amines behave like crystalloids, whereas higher amines (*e.g.* $C_{16}H_{38}.NH_2$) do not raise the boiling point of water and behave like colloids.

[2] Cp. also A. Müller, *Allgemeine Chemie der Kolloide*, 1907, 179.

[3] Cp. Kahlenberg and Schreiner, *Zeits. f. physik. Chem.*, 1898 (27), 552. Krafft, *Berichte*, 1899, 1584. A. Smits, *Zeits. f. physik. Chem.*, 1903 (45), 5. Krafft, *Zeits. f. angew. Chem.*, 1905, 857; *Zeits. f. physik. Chem.*, 1906 (47), 5. Kahlenberg, *Chem. Zeit.*, 1908, 689. A. Mayer, G. Schaeffer, and E. F. Terroine, *Compt. rend.*, 1908 (146), 484. With regard to the viscosity of aqueous solutions of sodium palmitate cp. F. D. Farrow, *Journ. Chem. Soc.*, 1912, 357. The viscosity of soap solutions—obtained from a "Marseilles soap," *i.e.* a mixture of sodium, salts of saturated and unsaturated fatty acids—is also dealt with by F. Bottazzi and C. Victorow, *Rendiconti del R. Accad. dei Lincei*, 1910, xix. I. 659.

[4] *Berichte*, 1910, 321; cp. also J. W. M'Bain, E. C. V. Cornish, and R. C. Bowden, "Studies of the Constitution of Soap in Solution: Sodium Myristate and Sodium Laurate," *Journ. Chem. Soc.*, 1912, 2042.

[5] *Zeits. f. physiol. Chem.*, 1911 (76), 179. Cp. F. Goldschmidt and L. Weissmann, *Zeits. f. Elektrochem.*, 1912 (18), 380.

Since, according to modern views, the difference between the colloidal state and complete solution, *i.e.* the crystalloidal state, is only one of degree,[2] there is no difficulty in accepting the view that soap behaves under some conditions like a colloid and under other conditions like a crystalloid, the special condition being chiefly the quantity of the solvent (" disperse phase ") in which the soap is suspended or distributed (" dispersed "). *Bowden*[3] expresses the opinion that the concentrated solutions may contain the acid salts in the colloidal state.

Possibly the question could be decided experimentally by studying the osmotic pressure of soap solutions of different concentrations, since all evidence goes to show that true solutions exhibit a definite osmotic pressure, whereas colloidal solutions show either no pressure or only a very slight one.

In this connection attention may be drawn to the important experiments made by *Kahlenberg*[4] and his collaborators which prove that instantaneous chemical changes take place in solutions of copper oleate in benzene on adding hydrochloric acid or stannic chloride, or on passing hydrogen sulphide gas through the solution. It was even found that it is possible in such solutions to replace one metal by another.

The hydrolytic action of water is retarded by the presence of free **alkali**. The following table, due to *Alder Wright and Thompson*, which should be compared with the one given above, p. 126, clearly illustrates this well-known fact (*Practice of Soap-making ;* cp. Vol. III. Chap. XV. " Soap Manufacture ").

Fatty Acids.	Excess of Na_2O added to Solution per 100 of Combined Soap.	Hydrolysis brought about by x Molecules of Water.		
	Per cent.	$x=150$	$x=250$	$x=2000$
Crude lauric	11·0	1·1	1·6	2·0
Cotton seed oil acids . .	15·0	nil	nil	6·5
Stearic and oleic (from tallow)	20·0	nil	nil	nil

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[1] "Contributions à l'Étude les Savons," Eighth International Congress, vol. xxii. 221.

[2] The size of particles in the crystalloidal state may be taken as falling approximately below 1$\mu\mu$, whilst those representing the colloidal state would fall between 0·1μ and 1$\mu\mu$.

[3] *Journ. Chem. Soc.*, 1911, 193 ; cp. also F. G. Donnan and A. S. White, *ibid.*, 1911, 1668.

[4] Instantaneous chemical reactions and the theory of electrolytic dissociation, *Journ. Phys. Chem.*, 1902 (6), 1 ; cp. J. L. Sammis, *ibid.*, 1906 (10), 593.

Alcohol also exercises a retarding influence on the hydrolysis of soaps. Absolute alcohol, as also alcohol of 95 to 90 per cent, dissolve neutral soaps without causing dissociation. This is proved by the following table, which I have collated from *Krafft's*[1] determinations of the molecular weights of normal soaps in solutions of anhydrous alcohol.

Salt.	Formula.	Molecular Weight found.	Theoretical Molecular Weight.
Potassium formate . .	CHO_2K	87·60	84·16
,, acetate . .	$C_2H_3O_2K$	93·3-96·7	98·18
(Potassium heptylate . .	$C_7H_{13}O_2K$	153·7-156·5	168·28)
Sodium laurate . . .	$C_{12}H_{23}O_2Na$	237·2	222·3
,, myristate . .	$C_{14}H_{27}O_2Na$	253	250·3
,, palmitate . .	$C_{16}H_{31}O_2Na$	282·6	278·4
,, oleate . . .	$C_{18}H_{33}O_2Na$	301·3-345·9	304·4
Rubidium palmitate . .	$C_{16}H_{31}O_2Rb$	339·6	340·6
,, stearate . .	$C_{18}H_{35}O_2Rb$	369·0	368·7
Caesium palmitate . .	$C_{16}H_{31}O_2Cs$	387·9	388·2
,, stearate . . .	$C_{18}H_{35}O_2Cs$	415·5	416·3
Potassium oleate . . .	$C_{18}H_{33}O_2K$	347	320

If water be added to an alcoholic soap solution, hydrolysis is brought about, in proportion to the quantity of water added. (This is easily demonstrated by adding a drop of phenolphthalein solution.) *Kanitz*[2] showed that in order to prevent hydrolysis an alcoholic soap solution must contain at least 40 per cent of absolute alcohol. In practice it is safer to work with higher concentrations.[3] Soaps separate from their concentrated alcoholic solutions, on cooling, as a jelly-like mass, which, however, becomes crystalline on standing for some time.

With regard to the solubilities in alcohol of the soaps of the individual fatty acids, compare the statements under the several acids in this chapter[4] (see below).

Alkaline alcoholic soap solutions containing so much alcohol that no dissociation takes place are decomposed to a considerable extent in the cold by a current of carbon dioxide.[5]

Amyl alcohol if present to the extent of at least 15 per cent prevents hydrolysis of soap solutions.

Glycerol also causes a diminution of the amount of hydrolysis brought about by water.

The presence of **salts** diminishes the solubility of soaps in water. Soaps are insoluble in sufficiently concentrated solutions of common salt, of sodium sulphate, and of caustic alkalis. The soaps are therefore thrown out of their aqueous solutions by the addition of salt, etc. (*Soap-making*; cp. Vol. III. Chap. XV. "Soap Manufacture"). The laurates and ricinoleates are remarkable in this respect, as they require large quantities of salt to throw them out of their solutions.

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[1] *Berichte*, 1899, 1594; *Zeits. f. physiol. Chem.*, 1906 (47). 1.

[2] *Berichte*, 1903, 400.

[3] Cp. Holde, *Zeits. f. Elektrochemie*, 1910, 438.

[4] Cp. also Freundlich, *Chem. Revue*, 1908, 135; 160.

[5] Fendler and Kuhn, *Zeits. f. angew. Chem.*, 1909, 107.

Stiepel[1] examined the behaviour of the sodium salts of caproic, caprylic, capric, lauric, myristic, palmitic, and stearic acids to solutions of common salt. Whereas sodium caproate is not "salted out" from its solution by a saturated solution of sodium chloride, the laurate is insoluble in a 17 per cent, and the stearate in a 5 per cent, solution of sodium chloride.

The affinities of those fatty acids, which are most frequently met in natural oils and fats, to **caustic soda and potash** are sensibly the same; hence if a mixture of caustic soda and potash be brought into contact with a quantity of fatty acids which is insufficient to neutralise the total alkali present, a mixture of soda and potash soaps results with an excess of caustic alkali, and the ratio between free caustic soda and potash is approximately the same as that of the combined alkalis. The following table, due to *Alder Wright and Thompson*,[2] expresses this clearly; in each experiment there were present for one molecule of fatty acid two molecules of alkali, one of caustic soda, and one of caustic potash:—

Fatty Acid.	Percentage of Total Fatty Acid converted into	
	Soda Soap.	Potash Soap.
Pure stearic	51·2	48·8
Pure oleic	50·8	49·2
Crude stearic and oleic (tallow) . .	51·5	48·5
Crude stearic, palmitic, and oleic (palm oil and tallow) . . .	48·2	51·8
Crude lauric (cocoa nut oil) . .	49·7	50·3
Mean . .	50·3	49·7

Practically, in every case half the caustic alkali was present as soap and the other half as uncombined hydroxide (cp. also Chap. II. p. 99). The experiments thus bear out the logical postulate, that a soda soap on treatment with as much caustic potash as is equivalent to the soda present, and conversely, a potash soap treated with one equivalent of caustic soda, should yield a soap containing half the fatty acid in combination with potash and the other half combined with soda.

The **carbonates** of soda and potash behave in a manner very different from that of the caustic alkalis. Experiments carried out in a similar fashion to those described in the case of the caustic alkalis proved that the prevailing tendency is towards the formation of potash soap and sodium carbonate, whether potassium carbonate be intermixed with soda soap in proportions equivalent to the base, or sodium carbonate be intermixed with potash soap; in the latter case, even when the quantity of sodium carbonate was largely in excess of the amount equivalent to the potash present, only a comparatively small proportion of soda soap was formed. The following table, due to *Alder Wright and Thompson*, gives the actual numbers obtained :—

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[1] *Seifenfabrikant*, 1901, 933.

[2] *Journ. Soc. Chem. Ind.*, 1885, 626.

Fatty Acid.	Soda Soap fused with CO_3K_2. Percentage of Total Fatty Acids present.		Potash Soaps fused with CO_3Na_2. Percentage of Total Fatty Acids present.	
	Equivalent to the CO_3K_2 added.	Actually converted into Potash Soap.	Equivalent to the CO_3Na_2 added.	Actually converted into Soda Soap.
Stearic and oleic (tallow) . .	10·4	8·0		
,, ,,	45·7	34·4		
,, ,,	100·0	97·95	100·0	4·3
,, ,,	104·2	99·00	1000	15·0
Stearic, palmitic, and oleic (palm oil and tallow). . . .	57·2	52·1		
Stearic, palmitic, and oleic (palm oil and tallow). . . .	108·0	90·8	177·0	9·5
Crude lauric (cocoa nut oil) . .	52·8	46·4		
,, ,,	114·8	87·9	197·0	6·2
Crude ricinoleic (castor oil) . .	50·0	48·4		
,, ,,	100·0	93·8	205·0	8·2

The **chlorides** of the alkali-metals behave in the reverse manner, the prevailing tendency being towards the formation of soda soap and potassium chloride ; at any rate, these salts are formed in preference to potash soap and sodium chloride when the relative masses are nearly equal. (*Old method of making hard soap from wood ashes* ; cp. Vol. III. Chap. XV. "Soap Manufacture.") On repeating the same operation, the exchange of the metals may become a complete one.

The results obtained by *Alder Wright and Thompson* in a series of experiments, where 10 molecules of KCl and 10 molecules of NaCl were used for 1 molecule of soap represented by one-half molecule of potash soap and one-half molecule of soda soap, are reproduced in the following table :—

Fatty Acid.	Percentage of Fatty Acid contained		Molecular Ratio of Soda Soap to Potash Soap.
	As Potash Soap.	As Soda Soap.	
Pure oleic	38·0	62·0	1·63 : 1
Crude ricinoleic (from castor oil)	17·8	82·2	4·6 : 1
Stearic, oleic, and rosin (from tallow-rosin soap) . .	17·2	82·8	4·8 : 1
Crude lauric (from cocoa nut oil soap)	15·1	85·9	5·7 : 1

However, by modifying the relative masses, potash soap and sodium chloride can be produced. The experimental proof is furnished by the figures of the following table, where, in the case of columns (*a*), potash soaps dissolved in M molecules of water were salted out by

N molecules of sodium chloride for 1 molecule of soap, and in the case of columns (*b*), soda soaps dissolved in M molecules of water were salted out by adding N molecules of potassium chloride for 1 molecule of soap.

Fatty Acid.	M	N	(*a*) Potash Soaps salted out with NaCl. Percentage of Fatty Acid in Curd as		(*b*) Soda Soaps salted out with KCl. Percentage of Fatty Acid in Curd as	
			Potash Soap.	Soda Soap.	Potash Soap.	Soda Soap.
Stearic and oleic (from tallow)	100	5	10·5	89·5	79·1	20·9
,, ,,	200	20	5·1	94·9	82·1	17·9
Stearic, palmitic, and oleic (from palm oil and tallow)	200	20	3·8	96·2	95·8	4·2
Crude lauric (from cocoa nut oil)	200	20	5·4	94·6	74·8	25·2

Sulphates, although tending in the same direction, have a lesser "salting out" effect than sodium chloride. The greater solubility of sodium sulphate in water than that of chlorides explains this behaviour.

The action of chlorides and sulphates explains why caustic soda lyes (or alkaline lyes) containing chlorides and sulphates are less effective in promoting saponification than lyes free from it.[1]

The *density* of some solutions of sodium palmitate and sodium stearate at 90° C. (compared with water at 4° C.) is less than that of water. This is shown clearly by the following table due to *E. C. V. Cornish*:[2]—

Solutions.	Normality.	Density at 90°/4°.
Water	..	0·9653
Sodium hydroxide . . .	2·0 normal	1·0437
Sodium acetate . . .	1·0 ,,	1·0020
Sodium palmitate . .	1·0 ,,	0·9625
	0·5 ,,	0·9638
	0·35 ,,	0·9624
	0·2 ,,	0·9658
	0·1 ,,	0·9654
	0·05 ,,	0·9655
	0·01 ,,	0·9655
Sodium stearate . .	0·5 ,,	0·9599
	0·2 ,,	0·9631
	0·1 ,,	0·9629
	0·05 ,,	0·9621
	0·01 ,,	0·9639
Sodium palmitate with an equivalent excess of sodium hydroxide . . .	1·0 ,, Na	0·9796
	0·1 ,, ,,	0·9654
	0·02 ,, ,,	0·9646
Sodium palmitate with three equivalents excess of sodium hydroxide . . .	0·8 ,, ,,	0·9883
	0·4 ,, ,,	0·97935
	0·2 ,, ,,	0·9698

---

[1] Cp. Lewkowitsch, "Modern Views on the Constitution of Soap," *Journ. Soc. Chem. Ind.*, 1907, 590.

[2] *Zeits. f. phys. Chem.*, 1911 (76), 210.

The neutral soaps of the alkali metals are not readily soluble in the *organic solvents* (with the exception of alcohol) usually employed in analysis, such as ether, petroleum ether, benzene, etc. In the anhydrous state, the soaps are more soluble in ether and in benzene than in petroleum ether. On shaking out aqueous solutions of soaps, the soaps dissolve to a slight extent in ether, less so in petroleum ether. Acid soaps behave somewhat differently. As the solubility of soaps in organic solvents plays an important part in commercial analysis, these points will be considered fully in Chapter VI. ("Unsaponifiable Matter").

With regard to the behaviour of the sodium salts of the fatty acids on melting cp. *D. Vorlaender.*[1]

Lithium Salts.—The following solubilities were determined by *Partheil and Ferié* :[2]—

	100 c.c. Water dissolve at		100 c.c. Alcohol (spec. grav. 0·797) dissolve at	
	18° C.	25° C.	18° C.	25° C.
	Grms.	Grms.	Grms.	Grms.
Lithium laurate . .	0·158	0·176	0·418	0·4424
,, myristate .	0·0235	0·0234	0·184	0·22
,, palmitate .	0·011	0·018	0·0796	0·0955
,, stearate . .	0·01	0·012	0·041	0·0532
,, oleate . .	0·0674	0·132	0·9084	1·009

Ammonia Soaps

The *ammonium salts* of the fatty acids are obtained by saturating fatty acids with ammonia. The dissociation of the ammonia soaps[3] in aqueous solutions takes place at a much increased ratio as compared with the alkali metal salts. Aqueous solutions lose ammonia very readily on warming, hence neutral ammonia soaps cannot be prepared on a practical scale. When an ammonia soap is allowed to stand under a bell jar over concentrated sulphuric acid, ammonia is lost rapidly, until the amount left equals one-half of that present in the neutral soap. On further standing, the acid soap so obtained usually loses more ammonia, but far less rapidly than does the original neutral salt. The acid ammonium salts of stearic and lauric acids appear under these conditions to be considerably less unstable than those of oleic and ricinoleic acids (cp. also Vol. III. Chap. XV.).

The following table gives the solubilities of the ammonium salts of stearic, palmitic, and oleic acids in alcohol, ether, and acetone, as determined by *Falciola* :[4]—

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[1] *Berichte*, 1910, 3120.

[2] *Arch. d. Pharm.*, 1903, 552.

[3] Ammonia soaps are already mentioned by Darcet in the "Rapport" to the French Government, 1797.

[4] *Gazz. Chim.*, 1910 (40), 217.

Solubility in Alcohol ; Grams in 100 c.c. of Solvent

		Ammonium Salt of		
		Palmitic Acid.	Stearic Acid.	Oleic Acid.
Absolute Alcohol, at °C.	50°	11·0	5·5	100·0
	40°	4·5	1·8	. .
	30°	. .	0·9	. .
	20°	1·4	0·5	. .
	10°	0·7	0·3	59·0
75 per cent Alcohol, at °C.	40°	14·84	5·0	. .
	30°	11·02	1·83	10·86
	20°	4·33	. .	. .
	10°	1·78	0·56	8·20
50 per cent Alcohol, at °C.	40°	6·69	3·21	. .
	30°	. .	1·16	. .
	20°	5·33	0·51	. .
	10°	. .	0·25	. .

Solubility in Ether and Acetone at the ordinary temperature ; Grams in 100 c.c. of Solvent

	Ammonium Salt of		
	Palmitic Acid.	Stearic Acid.	Oleic Acid.
Ether . . .	0·29	0·1	16·9
Acetone . .	0·20 at 13° C.	0·08	4·7

With regard to the electrical conductivity and viscosity of ammonium soap solutions cp. *F. Goldschmidt and L. Weissmann.*[1]

(2) *Salts of the Alkaline Earths and of the Heavy Metals – Water-insoluble Soaps*

The salts falling under this head are best prepared by precipitating aqueous or alcoholic solutions of the ammonium or alkali metal salts with solutions of metallic acetates (cp. Vol. III. Chap. XV. " Metallic Soaps "). A systematic study of the solubilities in the usual solvents is still wanting ; an investigation should well repay the time required for it, as new methods of separating fatty acids could be elaborated.

The salts of the lowest fatty acids are soluble in water ; they readily form basic salts which separate out from these solutions on boiling.

The solubility of the salts decreases, like the solubility of the free acids, from butyric acid upwards, with the increase of the number of carbon atoms in the molecule. The numbers for the solubility of the *calcium salts* in water given in the following table demonstrate this clearly :—

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[1] *Zeit. Chem. Ind. d. Kolloide*, 1913 (12), 18.

Calcium Salt of	Soluble in parts of Water:	At Temperature. ° C.
Butyric acid . . .	3·5	14
Valeric acid . . .	4·9	20
Caproic acid . . .	4·4	21-22
Caprylic acid. . .	more than 160·0	20
Capric acid . . .	large quantity of water	100
Lauric acid . . .	about 2000	100

The calcium salts of the solid fatty acids are decomposed on heating to 270° C. The first product of decomposition of calcium palmitate or stearate is a mixture of solid (paraffin wax) and highly viscous hydrocarbons [1] (cp. also below, " Behaviour with Reagents ").

The *barium salts* (*Chevreul*) of the volatile acids, as also their *magnesium* [2] *salts* (*Ewers*) and *lead salts* (*Asbóth* [3]), are to some extent soluble in water ; in these cases also their solubility corresponds approximately to the solubility of the volatile acids themselves. The barium and calcium salts of the higher fatty acids are hydrolysed by water (cp. Palmitic acid, p. 160 ; Stearic acid, p. 165). On being subjected to dry distillation they yield, amongst other products, ketones (see p. 150).

Most salts of the lower fatty acids are soluble in alcohol ; those of the higher acids are insoluble in this menstruum. They are soluble to a considerable extent in hydrocarbons (see Vol. III. Chap. XV. " Metallic Soaps ").

The higher fatty acids, such as stearic, palmitic, and oleic, react slowly with copper, lead, zinc, cadmium, with evolution of hydrogen. Silver acts very slowly. Aluminium, nickel, cobalt, antimony, iron, bismuth, tin, mercury, and platinum remain apparently unaffected.[4]

The *lead salts* of the higher saturated acids [5] are nearly insoluble in ether, whereas lead oleate, lead linoleate,[6] lead ricinoleate,[6] in short, the lead salts of the most frequently occurring unsaturated acids, are soluble. The lead salt of erucic acid is but sparingly soluble in ether ; the lead salt of " iso-oleic " (see p. 192) acid is stated to be insoluble. The lead salt of ricinoleic acid is insoluble in low-boiling petroleum ether.

The solubilities of the lead salts of the following fatty acids in ether and petroleum ether have been studied by *G. B. Neave.*[7]

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[1] Künkler and Schwedhelm, *Augsb. Seifens. Zeit.*, 1908, 1286 ; 1341.

[2] Magnesium oleate appears to adsorb and carry down with it sodium oleate from solutions containing the latter ; sodium salts of saturated fatty acids are not so adsorbed (H. Masters and H. L. Smith, *Proc. Chem. Soc.*, 1913, 76).

[3] Cp., however, footnote 5, p. 525.

[4] C. B. Gates, *Journ. Phys. Chem.*, 1911 (15), 141.

[5] With regard to the lead salts of lower fatty acids cp. Colson, *Compt. rend.*, 1903, 675.

[6] Lead linoleate and lead ricinoleate denote here the salts of the mixed fatty acids from linseed and castor oils respectively.

[7] *Analyst*, 1912, 399.

[TABLE

Lead Salt of	Melting Point. °C.	100 c.c. of Solvent dissolve Grammes.			
		Ether.		Petroleum Ether boiling from 40-60° C.	
		At 20° C.	At Boiling Point.	At 20° C.	At Boiling Point.
Caproic acid .	73-74	..	1·3640	..	0·0608
(Heptylic acid .	90·5-91·5	0·2397	1·4900	0·0200	0·0528)
Caprylic acid .	83·5-84·5	0·0938	0·5460	Practically insoluble	0·0384
(Nonylic acid .	94-95	0·1115	0·2404	Practically insoluble	0·0450)
Capric acid .	100	0·0290	0·4285	Practically insoluble	0·0170
Lauric acid .	103-104	Practically insoluble	0·0205	Practically insoluble	Practically insoluble
Myristic acid .	107	Practically insoluble	0·0555	Practically insoluble	0·0210
Palmitic acid[1] .	112	Practically insoluble	0·0261	Practically insoluble	Practically insoluble
Stearic acid[1] .	125	Practically insoluble	Practically insoluble	Practically insoluble	0·0170
Oleic acid . .	45-50	Readily soluble	Readily soluble	Readily soluble	Readily soluble

Silver Salts.—The following solubilities of silver salts at 20° C. were determined by *O. Jensen* :[2]—

Silver	In 100 c.c. of Water.	In 100 c.c. 1/20 Norm. Silver Nitrate Solution.
	Grms.	Grms.
Butyrate . .	0·489	0·347
Caprate . . .	0·089	0·029
Caprylate . .	0·018	0·005

This table would seem to show that the solubility of the salts decreases with the excess of added silver nitrate.

Cadmium Salts.[3]—The cadmium salts of butyric and caproic acids are readily soluble in water. The cadmium salt of caprylic acid is less soluble and is precipitated to some extent—11 to 13 per cent—in concentrations of 0·025 to 0·050 grm. of acid in 50 c.c. of water. At a concentration of 0·1 grm. in 50 c.c., 63 per cent of the acid is precipitated as cadmium salt. Capric acid in the above concentrations is precipitated respectively to the extent of 83·6 per cent, 90·5 and 98·7 per cent. Lauric acid is almost completely precipitated, namely, in the order of the above concentrations to the extent of 94·9 per cent, 96·7 per cent, and 99·3 per cent.

Further information will be found under the headings of the individual acids in this chapter, in Chapter VIII., and Vol. III. Chap. XV. "Metallic Soaps."

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[1] Cp. also Chap. VIII. p. 543.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, x. 266.

[3] Paal and Amberger, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 33.

BEHAVIOUR WITH REAGENTS

The action of reagents on fatty acids is similar to that on their glycerides, excepting, of course, those chemical changes which are involved in hydrolysis. As the natural oils and fats contain glycerides of saturated acids in association with those of unsaturated fatty acids, the action of reagents on the mixed fatty acids as separated from the natural oils and fats is somewhat more complicated than in the case of the individual fatty acids. In the following lines an attempt will be made to distinguish the action which reagents have on *saturated* from that on *unsaturated* fatty acids; the special reactions characteristic of the several series of unsaturated fatty acids (cp. p. 111) will be considered under the headings of these several series.

The higher fatty acids, above lauric acid (see Chap. VIII.), can be freed from adhering water by drying at 100° C. The saturated acids do not absorb oxygen under these conditions; the unsaturated acids, however, must be dried *in vacuo* or in an atmosphere of an indifferent gas (see Chap. VIII. " Insoluble Fatty Acids ").

In the case of some hydroxylated acids, such as ricinoleic acid, polymerisation products are formed. I have shown[1] that in the case of wool wax fatty acids dehydration takes place to a considerable extent at 100° C., no doubt owing to the formation of lactones. The formation of a lactone at the ordinary temperature may be exemplified by γ-stearolactone, which is obtained on decomposing the potassium salt of γ-hydroxystearic acid with mineral acids.

When the non-volatile acids are heated to high temperatures, destructive distillation sets in with the formation of hydrocarbons. On heating the higher saturated fatty acids with *sodium*, *magnesium*, *aluminium*, *iron*, or *tin*, to a temperature of 350° C., there are formed carbon dioxide, hydrogen, gaseous hydrocarbons, and olefinic hydrocarbons having 22 to 28 carbon atoms in their molecule. Under the same conditions, *silver* and *copper* decompose the fatty acids to a very slight extent only (*Hébert*[2]).

On distilling stearic acid with magnesium powder at the lowest possible temperature, *Hébert* obtained stearone in admixture with solid and liquid hydrocarbons. *T. H. Easterfield and C. M. Taylor*[3] observed that when stearic acid is heated with one-tenth of its weight of sifted cast-iron turnings to 280° C., evolution of carbon dioxide becomes noticeable, and on raising the temperature to 370° C., stearone is formed to the extent of 80 per cent of the theoretical yield.[4] It would appear that a ferrous salt is first formed, and that this then undergoes decomposition; but on heating ferrous stearate to 360° C., only 60 per cent of stearone was obtained.

By heating oleic, elaïdic, erucic, brassidic, cerotic, melissic, and montanic acids with finely divided iron in the same manner, oleone, claïdone, crucicone, brassidone, cerotone, melissone, and montanone, respectively, were obtained. By employing aluminium or manganese in place of iron, 65 per cent of stearone is formed.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 141; 1896, 14.

[2] Hébert, *Bull. Soc. Chim.*, 1903, 316; Easterfield and Taylor, *Journ. Chem. Soc.* 1911, 2299.

[3] *Journ. Chem. Soc.*, 1911, 2299.

[4] English patent 7619, 1911; German patent 259,191.

In the case of the lower fatty acids, up to acids of 12 carbon atoms, the reaction is less complicated; ketones, which in their turn yield hydrocarbons, standing in near relation to the fatty acids from which they are derived.[1]

Mailhé [2] studied the action of acetic, propionic, butyric, and caprylic acids on *zinc dust* at temperatures ranging between 300° and 350° C. The decomposition taking place was not of a pyrogenic nature, inasmuch as the products contained the same number of carbon atoms as did the original material, or were secondary products derived from the products first formed; hence no far-reaching destruction took place. Nickel acted very energetically, but copper exercised a much less pronounced action.

Easterfield and Taylor also observed that ketones are the chief products of the interaction of the vapours of the lower fatty acids (from acetic up to, and including, caprylic acid) with many reduced metals.

The behaviour of unsaturated fatty acids under similar conditions has not been studied hitherto systematically (cp. "Oleic Acid," p. 186).

The fatty acids of the saturated series are not affected by the *oxygen* of air at the ordinary temperature. Mild oxidising agents such as hydrogen peroxide are, however, capable of oxidising all saturated fatty acids from formic acid up to, and including, stearic acid at a somewhat low temperature to ketones (cp. p. 55). The following table enumerates the ketones hitherto obtained by *Dakin* [3] from the fatty acids enumerated in the first column:—

Acid.	Product of Oxidation.
n-Butyric	Acetone
n-Valeric	Ethylmethylketone
Caproic	Propylmethylketone
Caprylic	Amylmethylketone
Nonylic	Hexylmethylketone
Capric	Heptylmethylketone
Lauric	Nonylmethylketone
Myristic	Undecylmethylketone
Palmitic	Tridecylmethylketone
Stearic	Quindecylmethylketone

The acids belonging to the linolic, linolenic, and especially the clupanodonic series absorb oxygen from the atmosphere at the ordinary temperature, to form products the nature of which has not yet been fully investigated (cp. Chap. VIII., and Vol. III. Chap. XV. "Oxidised Oils"). The acids belonging to the oleic series absorb oxygen from the air very slowly at the ordinary temperature, but the absorption becomes pronounced at a somewhat elevated temperature (cp. "Oleic Acid," p. 181) with formation of fatty acids insoluble in petroleum ether. I have termed these acids, pending further investigation into their nature, *oxidised acids* (cp. Chap. VIII.).

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[1] Hébert, *Bull. Soc. Chim.*, 1903, 316.

[2] *Chem. Zeit.*, 1909, 242.

[3] *Amer. Chem. Journ.*, 1910 (44), 41.

Ozone or ozonised air is without action on saturated acids. The unsaturated fatty acids, however, absorb ozone quantitatively much in the same manner as stated above (p. 59) for the unsaturated glycerides, *i.e.* they absorb for each pair of doubly-linked carbon atoms one molecule of ozone (see below, p. 174). Thus oleic acid yields oleic acid ozonide, $C_{18}H_{34}O_5$, and linolenic acid yields linolenic acid ozonide of the composition $C_{18}H_{30}O_{11}$ (see p. 205).

If ozonising be effected in a solution of hexane, normal ozonides are formed; if, however, the acids be ozonised in a chloroform solution, perozonides are obtained, that is to say, one further atom of oxygen is taken up, the latter apparently being absorbed by the COOH group, to form a CO_3H group. Therefore, the perozonide of linolenic acid, like that of oleic, contains one oxygen atom more than the normal ozonide. The perozonides are converted into normal ozonides by shaking with a dilute solution of sodium bicarbonate.

On boiling with water ozonides are easily decomposed into aldehydes, the third oxygen atom (of the ozone molecule) forming with water hydrogen peroxide, which in its turn oxidises the aldehydes (as far as possible) to acids. This may be exemplified by the formulæ given below, p. 184).

Sulphur.—For the action of sulphur on fatty acids, cp. Chap. I. p. 61. According to the *Chemische Fabrik. vorm. Dr. H. Byk*,[1] fatty acids having more than one double bond or containing an hydroxyl group, such as ricinoleic acid, form a plastic mass on heating them to 155°-160° C.

Hydrogen is without action on saturated fatty acids. The unsaturated fatty acids can be reduced to the corresponding saturated fatty acids under the same conditions, as stated above (p. 59), for glycerides of unsaturated fatty acids.

Chlorine,[2] *bromine, iodine, and iodochloride* act much in the same manner on fatty acids as they do on the corresponding glycerides (see p. 60). It is, however, notable that tariric acid absorbs only two atoms of halogen.

Concentrated sulphuric acid dissolves saturated fatty acids with the formation of sulpho-compounds, which are readily dissociated, by boiling with water, into sulphuric acid and the original fatty acids (*Chevreul*).

Fremy[3] was the first to put forward the view that saturated fatty acids form addition products with sulphuric acid. An extensive examination of these products was made by *Hoogewerff and van Dorp*,[4] who give the following two alternative explanations for the formation of these compounds:—

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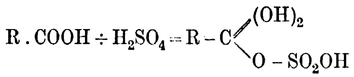
[1] German patent 252,193.

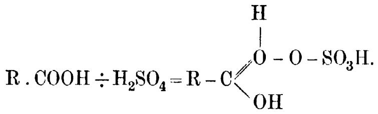
[2] For the preparation of monochlorinated fatty acids, by the action of sulphur chloride on fatty acids, see German patent 157,816 (H. Blank).

[3] *Ann. Pharm.*, 1836 (20), 50. [4] *Rec. trav. chim.* 18. 211, 1899; 21. 349, 1902.



$$R.COOH \div H_2SO_4 = R-C\begin{cases}(OH)_2\\O-SO_2OH\end{cases}$$

or



$$R.COOH \div H_2SO_4 = R-C\begin{cases}\overset{\displaystyle H}{\overset{|}{O}}-O-SO_3H.\\OH\end{cases}$$

B. W. van Eldik Thieme[1] prepared the addition product of lauric acid and sulphuric acid by heating lauric acid in a solution of 98·5 per cent sulphuric acid and allowing to crystallise. The crystals were found to consist of 1 molecule of lauric acid and 1½ molecules of sulphuric acid. This compound is soluble in cold petroleum ether. On diluting with more petroleum ether, however, the compound is dissociated.

The action of sulphuric acid on unsaturated acids is more complicated, as secondary products are formed (cp. below, p. 185).

Concentrated nitric acid oxidises all fatty acids, especially on prolonged boiling, carbon dioxide and dibasic acids being formed chiefly. In the case of capric acid *Lewkowitsch*[2] has shown that with concentrated nitric acid, as also with a mixture of concentrated nitric and sulphuric acids, carbonic and oxalic acids are obtained, and in the case of stearic acid, in addition to oxalic acid, suberic acid is formed. On prolonged boiling of myristic acid with nitric acid, specific gravity 1·3, the following dibasic acids are obtained: oxalic, succinic, glutaric, adipic, pimelic, and suberic.

Nitrous acid is without action on saturated acids; with unsaturated acids it behaves in a manner similar to that described above (p. 62); cp. also below, p. 173.

Nitrogen tetroxide.—For its action on unsaturated fatty acids see p. 174.

Selenious acid.—The action of selenious acid on some unsaturated fatty acids (as also their glycerides) has been made the subject of a (not yet completed) study by *S. Fokin.*[3]

Derivatives of Fatty Acids

Anhydrides of fatty acids corresponding to the formula $(R)_2O$ are obtained readily, as has been shown by *Lewkowitsch*,[4] in the case of capric, lauric, palmitic, stearic, cerotic, and oleic acids, by heating the fatty acids with acetic anhydride (cp. Chap. VI. "Acetyl Value"). Later on, *Albitzky* prepared palmitic and stearic anhydrides by heating the corresponding acids with acetic anhydride under pressure at 150°-160° C.

Kassler[5] patented the preparation of anhydrides from salts of fatty acids by means of sulphur chloride.

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[1] *Journ. f. prakt. Chem.*, 1912 (85), 298.

[2] *Ibid.*, 1879, 159.

[3] *Journ. Russ. Phys. Chem. Soc.*, 1913, 285.

[4] *Proc. Chem. Soc.*, 1890, 91.

[5] German patent 132,605, 1900.

The commercial production of anhydrides has been patented by *C. A. Jensen*[1] for *Th. Goldschmidt*, by *Goldschmidt* himself,[2] and by the *Akt. Ges. f. Anilin-Fabrikation.*[3]

For the separation of saturated fatty acids occurring in natural fats with the aid of their anhydrides (*Gsell*), see Chap. VIII. The following anhydrides have been obtained in a state of purity :—

Anhydride.	Boiling Point. °C.	Melting Point. °C.	Solidifying Point. °C
Acetic	137·9	...	...
Butyric	191-193	...	...
Valeric	215	...	...
Caproic	241-243	...	...
Caprylic	280-290	...	...
Lauric	...	42[4]	...
Myristic	...	51·5[4]	...
Palmitic	...	55-66[5]	56
Stearic	...	71-77[5]	68
Oleic	...	22-24	...
Elaïdic	...	49-51·5	...
Linolic[6]	...	...	...

Amido-derivatives.—By heating fatty acids in sealed tubes at temperatures near 200° C. with ammonia, aniline,[7] toluidine,[7] and naphthylamine,[7] their amides, anilides, toluidides, and naphthalides are formed. Some amido derivatives thus obtained are stated to have found technical application (cp. Vol. III. Chap. XV. " Amides of Fatty Acids "). The data collated by the author in the following table may therefore be found useful.[8]

Amides, Anilides, Toluidides, Naphthalides of Fatty Acids

Amides—	Melting Point. °C.
Acetic	82-83
Butyric	115
Valeric	114-116
Caproic	100
Caprylic	97-98
Capric	108
Lauric	110
Myristic	102
Palmitic	106-107
Stearic	108·5-109
Arachidic	108[9]
Behenic	111
Cerotic	109

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[1] English patent 25,433, 1908.

[2] English patent 611, 1911 ; French patent 407,046, and additions.

[3] English patent 23,924, 1910.

[4] Grün and Schacht, *Berichte*, 1907, 1782.

[5] Albitzky, *Journ. Russ. phys. chem. Soc.* 31, 477.

[6] H. Schoenfeld, *Inaug. Dissert.*, Zürich, 1912.

[7] Cp. Guérin, *Bull. Soc. Chim.*, 1903 [3], 29, 1117 ; P. W. Robertson, *Journ. Chem. Soc.*, 1908, 1033.

[8] As regards the action of furfuramide on fatty acids see Ludwig and Haupt, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiii. 605.

[9] Pickles and Hayworth obtained from arachidic acid (isolated from Niam Fat) an amide melting at 99° C. (*Analyst*, 1911, 494).

	Melting Point. °C.
Amides—	
Montanic	109-111 [1]
Melissic	116
Oleic	75-76
Elaïdic	93-94
Petroselinic	76
Erucic	84
Brassidic	90
Ricinoleic	66
Ricinelaïdic	91-93
Stearolic	78
Anilides—	
Caprylic	57
Capric	61
Lauric	68
Palmitic	90
Stearic	94
Cerotic	98·5 [1]
Montanic	101·5 [1]
Melissic	103 [1]
Stearolic	63
Toluidides—	
Butyric	74
Valeric	72
Caproic	75
Caprylic	67
Capric	80
Lauric	81-82
Myristic	93
Palmitic	66
Stearic	98
Naphthalides—	
Butyric	120
Valeric	111
Caproic	112
Caprylic	95
Capric	99
Lauric	100
Myristic	105
Palmitic	105
Stearic	110

Hydroxam-derivatives of fatty acids are obtained by warming glycerides with hydroxylamine chlorohydrate.[2] Thus stearo-hydroxamic and palmito-hydroxamic acids, $C_{17}H_{35}.C(OH):N.OH$ and $C_{15}H_{31}.C(OH):N.OH$, are prepared by warming stearin and palmitin respectively with hydroxylamine chlorohydrate.

Esters of fatty acids, other than glyceryl esters, are prepared by dissolving fatty acids in methyl-, ethyl-, amyl-, etc., alcohol, then passing a current of hydrochloric acid gas through the solutions and washing the product with water (cp. also Chap. XII.). As the methyl-esters, especially those of the higher fatty acids, are likely to play an important part in the examination of natural oils and fats (see Chap. XII.), and as the ethylesters of the higher saturated fatty acids may find technical application (in the manufacture of celluloid), the author has collated the following table :—

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[1] Th. Rigg, *Trans. New Zealand Inst.*, 1911, 64, 270.

[2] Morelli, *Atti R. Accad. dei Lincei*, 1908, 17. ii. 74.

Boiling Points and Melting Points of Methyl-, and Ethyl-esters of Fatty Acids [1]

Acid.	Methylester.		Ethylester.	
	Boiling Point. °C.	Melting Point. °C.	Boiling Point. °C.	Melting Point. °C.
Acetic	55	...	77	...
Butyric	102·3	...	119·9	...
Valeric	127·3	...	144·6	...
Caproic	149·6	...	165-166 under 735·8 mm. pressure	...
Caprylic	192·90 83 under 25 mm. pressure	−40 to −41	207-208	−47 to −48
Capric	223-224 114 under 15 mm. pressure	...	243-245	...
Lauric	148 under 18 mm. pressure	+5	269 71 *in vacuo*	−10
Myristic	167-168 under 15 mm. pressure	+18	295 102 *in vacuo*	−10·5 to −11·5
Palmitic	196 under 15 mm. pressure	28	122 *in vacuo*	...
Daturic	...	30	...	26·7
Stearic	214-215 under 15 mm. pressure	38	139 *in vacuo*	36·7
Arachidic	...	54·5	284-286 under 100 mm. pressure	50
Behenic	...	...	...	48-49
Lignoceric	...	56·5-57	305-310 under 15-20 mm. pressure	55
Carnaübic	...	54-55	...	49-50
Cerotic	...	60	...	59-60
Montanic	...	67-67·5	...	67
Melissic	...	74·5	...	73
Tiglic	...	...	156	...
Oleic	212-213 under 15 mm. pressure	...	...	...
Erucic	...	...	above 360	...
Brassidic	...	...	above 360	...
Linolic	207-208 under 11 mm. pressure	...	...	...
Chaulmoogric	227 under 20 mm. pressure	22	230 under 20 mm. pressure	...
Linolenic	207 under 14 mm. pressure	...	132-133 *in vacuo*	...
Ricinoleic	225-227 under 10 mm. pressure	...	227-230 under 10 mm. pressure	...
Dihydroxystearic	...	106-108	...	104-106
Japanic	...	...	...	53
Stearolic	204-206 under 20 mm. pressure	−3	215-216 under 20 mm. pressure	...

---

[1] The specific gravities are given under the headings of the individual fatty acids.

Ketones.—The preparation of ketones from fatty acids has been mentioned above (p. 144). The following list of ketones may prove useful. The lower ketones were obtained by the usual method of preparing ketones; the higher ketones by heating the fatty acids with iron filings to about 350° C.

Ketones.	Formula.	Melting Point °C.	Observer.
Caprone . . .	$(C_5H_{11})_2CO$	14·6	Lieben and Janecek [1]
Caprylone . . .	$(C_7H_{15})_2CO$	40	Guckelberger [2]
Caprinone . . .	$(C_9H_{19})_2CO$	58	Grimm [3]
Laurone . . .	$(C_{11}H_{23})_2CO$	69	Kipping [4]
Myristone [5] . . .	$(C_{13}H_{27})_2CO$	76·3	Krafft [6]
Palmitone . . .	$(C_{15}H_{31})_2CO$	82·8	,,
Daturone . . .	$(C_{16}H_{33})_2CO$	75·5-76	Gérard [7]
Stearone [8] . . .	$(C_{17}H_{35})_2CO$	87·8	Heintz [9]
Cerotone . . .	$(C_{25}H_{51})_2CO$	93	Th. Rigg [10]
Montanone . . .	$(C_{27}H_{55})_2CO$	97·5	,,
Melissone . . .	$(C_{29}H_{59})_2CO$	99·5-100	,,
Oleone [9] . . .	$(C_{17}H_{33})_2CO$	59	Easterfield and Taylor [11]
Elaïdone . . .	$(C_{17}H_{33})_2CO$	70	,,
Erucicone . . .	$(C_{21}H_{41})_2CO$	50-60	,,
Brassidone . . .	$(C_{21}H_{41})_2CO$	80	,,

I.—ACIDS OF THE ACETIC SERIES, $C_nH_{2n}O_2$

Formic acid is stated to occur in Strophantus seed oil, croton oil, macassar oil, egg oil, dadap fat, and in butter fat. These statements require, however, verification.

ACETIC ACID, $C_2H_4O_2 = CH_3.COOH$

The glyceride of this acid is stated to occur (undoubtedly as a mixed glyceride) in the seeds of the spindle tree, *Evonymus europæa*, L. Acetic acid has also been stated to occur in butter fat, macassar oil, and the fat from the seeds of *Brucea antidysenterica*. The properties of this acid need not be detailed here, inasmuch as the text-books on qualitative analysis supply the necessary information.

BUTYRIC ACID, $C_4H_8O_2 = CH_3.CH_2.CH_2.COOH$

Butyric acid was discovered by *Chevreul* in butter fat, in which it is found in the form of a mixed glyceride (to the extent of about 6 per cent).

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[1] *Liebig's Annal.* 187, 134.

[2] *Ibid.* 69, 201.

[3] *Ibid.* 157, 270.

[4] *Journ. Chem. Soc.* 57, 981.

[5] This ketone occurs naturally *in lucerne* (C. A. Jacobson, *Journ. Amer. Chem. Soc.*, 1911 (33), 2048).

[6] *Berichte*, 1882, 1713.

[7] *Annal. de Chim. et de Phys.* (6), 27, 563.

[8] For the occurrence of these ketones in the distillation products of fatty acids, cp. Vol. III. Chap. XV.

[9] *Jahresber. d. Chemie*, 1855, 515.

[10] *Trans. New Zealand Inst.*, 1911, 64, 270.

[11] *Journ. Chem. Soc.*, 1911, 2299.

Butyric acid at the ordinary temperature is a colourless liquid; the pure freshly distilled acid smells like acetic acid; its aqueous solution recalls the odour of rancid butter. It crystallises at −19° C.; the crystals melt at −6·5° C. (*Scheij*), −7·9° C. corr. (*Schneider*). The acid boils under ordinary pressure at 162·3° C.,[1] under 758 mm. pressure at 163°-164° C. (*Scheij*).

Konowalow determined the following boiling points for butyric acid solutions, under 740 mm. pressure:—

Butyric Acid. Per cent.	Water. Per cent.	Boiling Point. ° C.
74·52	25·48	98·44
50·00	50·00	98·95
29·90	71·10	99·97

G. Ryland[2] found that a mixture of 20 per cent water and 80 per cent of butyric acid under a pressure of 763 mm. has the constant boiling point of 99°-99·5° C.; in other words, the vapours have the same composition as the boiling liquid, so that a butyric acid solution of the above composition cannot be separated into its constituents by distillation.

$d^{0} = 0{\cdot}9746$; $d^{14} = 0{\cdot}958$; $d^{20^\circ}_{4^\circ}$ C. $= 0{\cdot}9590$; $d^{161{\cdot}5^\circ}_{4^\circ}$ C. $= 0{\cdot}8141$; $n^{20}_{D} =$ 1·39906 (*Scheij*).

Butyric acid is miscible with water, alcohol, and ether in all proportions. On adding calcium chloride or common salt to an aqueous solution, the acid separates in the form of oily drops. The aqueous solutions of butyric acid have a sour, burning taste, and show an acid reaction to litmus and phenolphthalein. Methylorange turns red in solutions of butyric acid free from butyrates (cp. p. 125).

On distilling a dilute aqueous solution of butyric acid the whole of the acid passes over into the distillate with the water vapours. If the acid is to be recovered from a dilute solution, it is best to neutralise with caustic soda, concentrate by evaporation, and then acidify with dilute sulphuric acid before distilling.

On warming an alcoholic solution of butyric acid with concentrated sulphuric acid, ethylbutyrate is formed; thus the smallest quantity of butyric acid may be recognised by the pleasant pine-apple odour of the ethylester. In dilute solutions butyric acid is detected by neutralising with caustic soda, evaporating to dryness, and warming the residue gently with alcohol and sulphuric acid. In oils and fats butyric acid is rapidly detected by treating with strong alcohol and an amount of caustic potash insufficient to effect complete saponification. (Qualitative detection of butter fat.) Chromic acid oxidises butyric acid to acetic acid and carbon dioxide. Alkaline permanganate oxidises it completely to carbonic acid and water (cp. Chapter VI. "Glycerol").

Butyric acid is prepared on a considerable scale by fermentation of cheese. It is largely used in the preparation of its ethylester (for flavouring), and is employed as such in tanneries[1] as a de-liming agent.

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[1] With regard to a condensation product, formed by distillation, see G. Albo, *Arch. scien. phys.*, Genève, 4 (12), 339.

[2] *Amer. Chem. Journ.*, 1899 (22), 384.

With the exception of the silver, mercurous, and lead salts, the metallic salts of butyric acid are *easily* soluble in water; the salts of the alkalis are deliquescent.

Calcium butyrate, $Ca(C_4H_7O_2)_2+H_2O$, is remarkable in that its solubility in water decreases with the increase of temperature. At 14° C. a saturated solution contains 1 part of the salt in 3½ parts of water. On warming to 30° C. a precipitate is obtained; and on boiling, the salt separates out, redissolving almost completely on cooling. The calcium salt is soluble in alcohol.

Barium butyrate, $Ba(C_4H_7O_2)_2+4H_2O$. 100 parts of water dissolve 37·5 parts of the anhydrous salt at temperatures from 0° to 40° C., and 35·9 parts from 40° to 82° C. 100 parts of absolute alcohol dissolve 0·126 part of the anhydrous salt.[2]

Silver butyrate, $AgC_4H_7O_2$, dissolves in 200 parts of water at 14° C. (see p. 152). It crystallises in needles or monoclinic prisms according to the concentration.

Methylester, $d^0{}_4=0{\cdot}92006$; boils at 102·3° C. under 760 mm.

Ethylester, solidifies at $-80°$ C.; $d^0{}_4=0{\cdot}89957$; boils at 119·9° C. under 760 mm

Isobutyric acid is stated by *Engelhardt* to occur in Japan wax (cp Vol. II. Chap. XIV.). This statement would appear to stand in need of confirmation; indeed *Tassily*[3] is of the opinion that the volatile fatty acid is pelargonic acid.

VALERIC ACID, $C_5H_{10}O_2$

Valeric acid is stated to occur as a glyceride—trivalerin—in porpoise and dolphin oils, the blubber oils from *Delphinus phocæna* and *Delphinus globiceps*. *Chevreul* discovered the acid ("phocenic acid") in 1817 in dolphin oil (and in 1818 in the berries of *Viburnum opulus*). The chemistry of the (dolphin oil) acid has not been investigated since then, and its occurrence in glycerides may be doubted. It is not unlikely that "valeric" acid is a mixture of butyric and caproic acids. The physical constants given here for "valeric" acid are those recorded for the normal acid $CH_3.CH_2.CH_2.CH_2.COOH$. Some justification for this may be found in the fact that *Marie* obtained normal valeric acid on oxidising stearic acid (see p. 165).

The odour of "valeric" acid resembles that of putrid cheese.

Normal valeric acid is a colourless liquid; it boils at 186° to 186·4° C. under 760 mm., at 184° to 185° C. under 736 mm. It solidifies at $-18°$ to $-20°$ C.[4]; $d^0=0{\cdot}9577$; $d^{20}=0{\cdot}9415$. It dissolves at 16° C. in 27 volumes of water; from this solution it is thrown up by calcium chloride.

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[1] T. Salomon, *Collegium*, 1912, 284.

[2] Cp. Wilcox, *Proc. Chem. Soc.*, 1895, 202.

[3] *Les Matières Grasses*, 1911, 2285.

[4] Massol (*Journ. Soc. Chem. Ind.*, 1895, 828; *Bull. Soc. Chim.* 13, 758) gives $-58{\cdot}5°$ C.

Methylester, d^0 = 0·9097. Boiling point 127·3° C.

Ethylester, d^0 = 0·894 ; at 20° C. = 0·8765. Boiling point 144·6° C.

CAPROIC ACID,[1] $C_6H_{12}O_2 = CH_3.CH_2.CH_2.CH_2.CH_2.COOH$

Caproic acid occurs, undoubtedly as a mixed glyceride, in butter fat (in which it was discovered by *Chevreul* in 1818), and in cocoa nut and palm nut oils. The acid is no longer miscible with water, although it is to some extent soluble in it; 100 c.c. dissolve 0·882 grm. at 15° C. It melts at −8° C. (*Scheij*) and boils at 202°-203° C. at 770 mm. pressure. $d^{20°}_{4°}$ C. = 0·924 ; n^{20}_{D} = 1·41635 (*Scheij*). Its odour is like that of sweat.

Ammonium caproate, $(NH_4)C_6H_{11}O_2$ (*Würtz; Falciola*[2]).

Calcium caproate crystallises with 1 molecule of water in laminæ $([C_6H_{11}O_2]_2Ca + H_2O)$; 100 parts of water dissolve 4·4 parts of the anhydrous salt at 21°-22° C. *Barium caproate* crystallises with 2 molecules of water $[(C_6H_{11}O_2)_2Ba + 2H_2O]$; 100 parts of water dissolve 11·1 parts of the anhydrous salt at 10·5° C. *Zinc caproate* is precipitated as a crystalline powder of the composition $(C_6H_{11}O_2)_2Zn + H_2O$ on pouring caproic acid into a zinc acetate solution. (Difference from butyric and valeric acids.) 100 parts of water dissolve 1·03 parts of the anhydrous salt at 34·5° C.

Copper caproate[3] when dried in air forms a fine blue powder; on being heated from 110° to 120° C. it suddenly turns green and remains green on cooling. Metallic lead easily precipitates metallic copper from a solution of copper caproate in pyridine.

Methylester, d^0 = 0·9309. Boiling point 149·6° C. under 760 mm. ; 52°-53° C. under 15 mm. (*Haller and Youssoufian*[4]).

Ethylester, d^0 = 0·8890 ; d^{20} = 0·8732 ; d^{40} = 0·8594. Boiling point 165·5°-166° C. under 735·8 mm.

CAPRYLIC ACID, $C_8H_{16}O_2 = CH_3.(CH_2)_6.COOH$

Caprylic acid occurs in butter fat (*Lerch* in 1844), and notably in cocoa nut and palm nut oils. This acid is just as characteristic of these two oils as is butyric acid of butter fat, and is best prepared from cocoa nut oil by fractionating its methylesters (*Guérin*). The acid is liquid at the ordinary temperature, and crystallises on cooling at 12° C. in laminæ melting at 16·5° C. ; it boils at 236°-237° C. under 761 mm., and at 123·5°-124·3° C. under 10 mm. d = 0·9270 at 0° C. ; $d^{20°}_{4°}$ = 0·9100 ; n^{20}_{D} = 1·42825. One part dissolves in 400 parts of boiling water; on cooling, the dissolved acid separates out almost completely. 100 c.c. of water at 15° C. hold in solution 0·079 grm. The acid has an intense odour of sweat.

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[1] This acid is frequently described as isobutylacetic acid (cp. also *Berichte*, 1907, 2548).

[2] *Gazz. chimica*, 1910, ii. 435.

[3] Kahlenberg, *Journ. phys. Chem.*, 1902 (6), 6 ; cp. also C. B. Gates, *Journ. phys. Chem.*, 1911 (15), 101.

[4] *Compt. rend.*, 1906 (143), 803.

Ammonium caprylate, $(NH_4)C_8H_{15}O_2$, melts between 70° and 85° C., and crystallises from benzene, on cooling. It is sparingly soluble in ether, carbon bisulphide, and carbon tetrachloride; very easily soluble in methyl alcohol, ethyl alcohol, and chloroform (*Falciola* [1]).

Barium caprylate, $Ba(C_8H_{15}O_2)_2$, crystallises in laminæ; 100 parts of water dissolve 0·619 parts at 20° C.

Lead caprylate, $(C_8H_{15}O_2)_2Pb$, crystallises from alcohol in laminæ melting at 83·5°-84·5° C.

Copper caprylate, $Cu(C_8H_{15}O_2)_2$, crystallises from alcohol in green laminæ melting at 264°-266° C.

Silver salt, see p. 152.

Methylester, $d^0 = 0·8942$; $d^{18} = 0·887$; solidifies at $-40°$ to $-41°$ C.; boils at 192°-194° C. under 760 mm., 95° C. under 25 mm. (*Guérin*), 83° C. under 15 mm. (*Haller and Youssoufian*).

Ethylester, $d^0 = 0·8842$; $d^{16} = 0·8730$; solidifying point, $-47°$ C. to $-48°$ C.; boiling point, 207°-208° C.

CAPRIC ACID, $C_{10}H_{20}O_2 = CH_3.(CH_2)_8.COOH$

Capric acid occurs in the milk fats of the cow (*Chevreul*) and the goat (*Lerch*), in the fat from *Lindera Benzoin*, in cocoa nut oil (*Görgey* [2]), palm nut oil, and in coffee berry oil. According to *Pawlenko* [3] elm seed oil (see Vol. II. Chap. XIV.) fatty acids consist to the extent of 50 per cent of capric acid. In wool yolk it occurs as a potassium salt.

Capric acid crystallises in fine needles, melting at 31·3°-31·4° C. (*Krafft* [4]), and boiling at 268°-270° C. under 760 mm. (*Grimm* [5]), 199·5°-200° C. under 100 mm., 153°-154° C. under 13 mm. (*Scheij*); $d^{37} = 0·930$; $d^{40°}_{4°} = 0·8858$; $n^{40}_{D} = 1·42855$.

The acid is almost insoluble in cold water; one part dissolves in about 1000 parts of boiling water. The acid has a goat-like smell, which becomes more distinct at its melting point.

The alkali caprates are easily soluble in water. *Barium caprate* is nearly insoluble in cold water, very sparingly soluble in boiling water, from which it crystallises in laminæ. It is easily soluble in boiling alcohol.

Methylester, boils at 223°-224° C. under 760 mm., and at 114° C. under 15 mm.; it solidifies at $-18°$ C.

Ethylester, specific gravity 0·862; boiling point 243°-245° C.

LAURIC ACID, $C_{12}H_{24}O_2$

Lauric acid is found in considerable quantities in kusu oil, tangkallak fat,[6] dika fat,[6] and laurel oil.[7] Cocoa nut oil,[8] palm nut oil, pichurim beans,[1] the fat from *Lindera Benzoin*,[2] shea butter, and spermaceti (?)[3] also contain notable proportions of laurin. Kusu oil consists for the most part of the triglyceride of lauric acid. The fatty acid occurring in the nuts of the Californian bay tree, *Umbellularia californica*, formerly described as umbellulic[4] acid, is true lauric acid. The acid is best prepared[5] from laurin obtained by recrystallising tangkallak fat from ether and saponifying that glyceride, or from cocoa nut oil by preparing the methylesters of its mixed fatty acids and fractionating them.[6]

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[1] *Gazz. chimica*, 1910, ii. 435.

[2] *Liebig's Annalen*, 1858 (66), 290.

[3] *Chem. Rev.*, 1912 (43).

[4] *Berichte*, 1882, 696; 1883, 1716.

[5] *Liebig's Annalen*, 1870 (157), 264.

[6] Oudemans, *Journ. f. prakt. Chem.*, 1860 [1], 81, 356; Lewkowitsch, *Analyst*, 1905, 394.

[7] Marsson, *Liebig's Annalen*, 1842 (41), 329; Krafft, *Berichte*, 1879 (12), 1665.

[8] Görgey, *Liebig's Annalen*, 1848 (66), 303; Oudemans, *Journ. f. prakt. Chem.*, 1860 (81), 375; Guérin, *Bull. Soc. Chim.*, 1903, 29 [3], 1117.

At the ordinary temperature the acid is solid; it crystallises from alcohol in needles melting at 43·6° C. Lauric acid is the first acid of the acetic series that cannot be distilled at ordinary pressure without undergoing (slight) decomposition. It boils at 225° C. under 100 mm., 176° C. under 15 mm., 102° C. *in vacuo*. $d^{20°}_{4°}$ C. = 0·883, $d^{43·6°}_{4°}$ C. = 0·875, $d^{60°}_{4°}$ C. = 0·8642; $d^{78·5°}_{4°}$ C. = 0·8495; $n^{60}_{D} = 1·42665$ (*Scheij*), $n^{76}_{D} = 1·4236$ (*Partheil and Ferié*).

Lauric acid is slightly soluble in large quantities of boiling water; on distilling its aqueous solution it passes over to an appreciable extent with the vapours. It has been repeatedly pointed out that lauric acid occupies an intermediate position between the soluble and the insoluble fatty acids. The laurates of the alkali metals differ from the corresponding salts of the higher fatty acids in that they require large quantities of salt for "salting out." (*Cocoa nut soaps, marine soaps*, see Vol. III. Chap. XV.)

Ammonium laurate, $NH_4C_{12}H_{23}O_2$, melts at 75° C. It is insoluble in cold water, forming therewith a foam, whilst very fine crystals separate. Absolute alcohol at 7° C. dissolves 4·8 per cent. It dissolves in methyl alcohol and crystallises from cold benzene; it is slightly soluble in ether and acetone (*Falciola*[7]).

The solubilities in water and alcohol of a number of metallic salts of lauric acid, due to *Oudemans*, are given in the following table :—

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[1] Sthamer, *Liebig's Annal.*, 1845 (53), 390.

[2] Caspari, *Amer. Chem. Journ.*, 1902 (27), 291.

[3] Heintz, *Journ. f. prakt. Chem.*, 1855 (66), 43.

[4] Stillmann and O'Neill, *Journ. Soc. Chem. Ind.*, 1883, 124. Cp. second edition of this work, p. 44.

[5] Cp. also Krafft, *Berichte*, 1879, 1665.

[6] Guérin, *Bull. Soc. Chim.*, 1903 [3], 29, 1117.

[7] *Gazz. chim.*, 1910, ii. 435.

Salt.	Formula.	1000 Parts of Water dissolve		1000 Parts of Alcohol dissolve	
		At the Boiling Point.	At 15° C.	At the Boiling Point.	At 15° C.
Magnesium laurate	$Mg\bar{A}_2+3H_2O$	0·411	0·230	126·0	15·25
Calcium laurate .	$Ca\bar{A}_2+H_2O$	0·547	0·039	22·02	0·719
Strontium laurate .	$Sr\bar{A}_2+H_2O$	0·360	0·272	3·59	9·598
Barium laurate .	$Ba\bar{A}_2$	0·698	0·054	1·009	0·187
Zinc laurate . .	$Zn\bar{A}_2+H_2O$ (?)	0·189	0·103	8·78	0·134
Lead laurate .	$Pb\bar{A}_2$	0·011	...	2·35	0·047
Manganese laurate	$Mn\bar{A}_2+xH_2O$	0·401	0·011	3·82	0·481
Cobalt laurate .	$Co\bar{A}_2+H_2O$	0·376	0·072	18·01	0·174
Nickel laurate .	$Ni\bar{A}_2+H_2O$ or $3H_2O$	0·390	0·197	6·68	0·640
Copper laurate[1] .	$Cu\bar{A}_2$	0·029	0·023	6·53	0·775
Silver laurate .	$Ag\bar{A}$	0·405	0·001	0·284	0·323
Lithium laurate[2] .	$Li\bar{A}$	Cp.	p. 139.		

Methylester, boils at 141° C. under 15 mm. (*Haller and Youssoufian*); 148° C. under 18 mm. pressure (*Guérin*); melting point, + 5° C.

Ethylester, $d^{19} = 0{\cdot}8671$; solidifying point, − 10° C. (*Görgey*); boils at 269° C. under 760 mm. (*Delffs*[3]); *in vacuo* at 79° C. if the vapours have to rise 25 mm., and 101° C. if the vapours have to rise 65 mm.[4]

FICOCERYLIC ACID, $C_{13}H_{26}O_2$[5]

Ficocerylic acid is the acid constituent of gondang wax; it melts at 57° C. The number of carbon atoms being uneven, a fresh examination of this acid would seem to be desirable; all the more so as a normal tridecylic acid[6] prepared from synthetical tridecylic alcohol melts at 40° C.

MYRISTIC ACID, $C_{14}H_{28}O_2$

This acid occurs in considerable quantities in all fats belonging to the "Myristica Group" (see Vol. II. Chap. XIV.), and was first discovered by *Playfair* in nutmeg butter.[7] Indeed, the acid may be considered as characteristic of all those fats that are enumerated in Vol. II. under this natural group. From "Virola fat"[8] the triglyceride of the acid can be easily isolated, and "Ochoco fat"[1] (Vol. II. Chap. XIV.) has been shown by the author[2] to consist of practically pure myristin. The two last-named fats would therefore furnish the best raw material for the preparation of myristic acid. To a smaller extent myristic acid is found in dika fat,[3] cocoa nut and palm nut oils, lard, linseed oil, canari oil,[4] quince oil, cod liver oil, sedge oil, arachis oil, butter fat, and the fat of cochineal.[5] It is also stated to occur as cetyl myristate in spermaceti and, in combination with unknown alcohols, in wool wax.[6] In very small quantities (0·04 per cent) it has also been found in the gall of oxen.[7]

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[1] The solubility of this salt in a number of solvents has been determined by C. B. Gates, *Journ. phys. Chem.*, 1911 (15), 101.

[2] Partheil and Ferié, *Arch. d. Pharm.*, 1903, 545.

[3] *Liebig's Annal.* 92, 278.

[4] Krafft, *Berichte*, 1903, 4340; cp. also Rechenberg, *Journ. f. prakt. Chem.*, 1909, (80), 475, and Krafft, *Journ. f. prakt. Chem.*, 1909 (80), 242.

[5] Greshoff and Sack, *Rec. d. trav. chim. Pays-Bas*, 1901, 65.

[6] Blau, *Monatsh. f. Chem.* 26, 89.

[7] *Liebig's Annal.*, 1841 (37), 152; cp. also Krafft, *Berichte*, 1879 (12), 1669.

[8] Thoms and Mannich, *Ber. d. d. pharm. Ges.*, 1901, 264.

Myristic acid crystallises in laminæ melting at 53·8° C., and boiling at 250·5° C. under 100 mm., at 196·5° C. under 15 mm., and at 121°-122° C. *in vacuo*. $d^{53\cdot8^\circ}_{4^\circ}$ C. = 0·8622 ; $d^{60^\circ}_{4^\circ}$ C. = 0·8584 ; $n^{60}_{D} = 1\cdot43075$, $n^{76\cdot5}_{D} = 1\cdot4248$.

The acid is completely insoluble in water ; when boiled with water at the pressure of 760 mm., about 7·7 per cent of the acid is carried over with the water vapour ; under a pressure of 38 mm. in a current of superheated steam at 168·5° C., the distillate contains 65·7 per cent of myristic acid. It dissolves with difficulty in cold alcohol and ether.

Ammonium myristate, $NH_4C_{14}H_{27}O_2$, melts between 75° and 90° C. It is sparingly soluble in cold acetone, but easily soluble in warm acetone. It is very sparingly soluble in cold as also in warm carbon bisulphide. It dissolves in warm benzene, and chloroform ; it is slightly soluble in methyl alcohol, more soluble in ethyl alcohol, especially at a somewhat elevated temperature (*Falciola*[8]).

Lithium myristate[9] crystallises from alcohol in the form of small white scales. 100 c.c. of water dissolve at 18° C. 0·0235 grm., and at 25° C. 0·0234 grm. of the salt. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·184 grm., and at 25° C. 0·22 grm.

Lead myristate is more readily soluble in ether than are the palmitate and stearate.

Barium myristate forms a crystalline powder, very sparingly soluble in water and alcohol.

Methylester, boils at 167°-168° C. under 15 mm. ; and at 295° C. under 751 mm. ; melting point, 18° C. (*Haller and Youssoufian*).[10]

Ethylester, boils at 295° C. under ordinary pressure, and *in vacuo* at 102° or 124° C., according as to whether the vapours have to rise 25 mm. or 65 mm. ; solidifies at 10·5°-11·5° C. Sparingly soluble in alcohol and ether, more readily soluble in petroleum ether.[11]

ISOCETIC ACID, $C_{15}H_{30}O_2$

The glyceride of this acid was stated by *Bouis* to occur in curcas oil (Vol. II. Chap. XIV.). The acid crystallises in laminæ, having the melting point 55° C. In view of the uneven number of carbon atoms its existence is doubtful.

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[1] Uricoechea, *Liebig's Annal.*, 1854 (91), 369 ; Reimer and Will, *Berichte*, 1885 (18), 2011 ; Nördlinger, *ibid.*, 1885 (18), 2617.

[2] Lewkowitsch, *Analyst*, 1908, 313.

[3] Oudemans, *Journ. f. prakt. Chem.*, 1860 (81), 356 ; 1866 (99), 409.

[4] See Vol. II. Chap. XIV. "Canari Oil."

[5] Liebermann, *Berichte*, 1885, 1982.

[6] Darmstaedter and Lifschütz, *ibid.*, 1896 (29), 618 ; 1898 (31), 97.

[7] Lassar-Cohn, *ibid.*, 1892 (25), 1829.

[8] *Gazz. chim.*, 1910, ii. 435.

[9] Partheil and Ferić, *Arch. d. Pharm.*, 1903, 545.

[10] Cp. also Bull, *Berichte*, 1906, 3572.

[11] Krafft, *ibid.*, 1903, 4340.

Okada[1] states that he obtained isocetic acid from Japan fish oil. In his opinion the isocetic acid differs from an acid of the same melting point as isolated from a mixture of palmitic and stearic acids, by its crystalline form. This statement stands greatly in need of confirmation.

PALMITIC ACID, $C_{16}H_{32}O_2$

Palmitic acid occurs in most vegetable and animal fats, notably in large quantities in palm oil, from which it was first isolated in a pure state,[2] in Chinese vegetable tallow,[3] Japan wax,[4] and myrtle wax.[5] It occurs also in spermaceti[6] as cetyl palmitate, in beeswax[7] as myricyl palmitate, and in opium wax as ceryl palmitate.

The artificial preparation of palmitic acid from oleic acid by melting the latter with caustic alkali seemed at one time to be important from a commercial[8] point of view. The reaction is generally stated to take place according to the following equation :—

$$C_{18}H_{34}O_2 + 2KOH = KC_{16}H_{31}O_2 + KC_2H_3O_2 + H_2,$$

but it should be noted that, besides considerable quantities of acetic acid, *Varrentrapp* found, as a by-product, oxalic acid in small quantities, whereas *Edmed*[9] states that oxalic acid is formed to a greater extent than acetic acid, the latter being obtained in extremely small quantities. Petroselinic acid also (see below, p. 193) yields palmitic and acetic acids by the same reaction.

Pure palmitic acid forms tufts of finely crystallised needles ; the melted acid solidifies on cooling to a nacreous, scaly, crystalline mass. The acid is free from smell or taste, and melts at 62·62° C. The solidifying point of a carefully purified specimen is given by *de Visser*[10] as 62·618° C. It boils between 339° and 356° C. with slight decomposition ; it distils unchanged under a pressure of 100 mm. at 271·5° C., under 15 mm. at 215° C., and *in vacuo* at 138°-139° C. $d^{62°}_{4°}$ C. = 0·8527 ; $d^{80°}_{4°}$ C. = 0·8412 ; $n^{74·5}_{D} = 1·4284$, $n^{80}_{D} = 1·42693$, $n^{60}_{D} = 1·4324$ (*Ruttan*).

Palmitic acid is not readily soluble in cold alcohol ; 100 c.c. of (methylated) alcohol of the specific gravity 0·8183 (containing 94·4 per cent of ethyl alcohol by volume), after having been kept at 0° C. for the number of hours stated in the following table, held the following quantities in solution (*Hehner and Mitchell*[11]) :—

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[1] *Chem. Zeit.*, 1908, 1199.

[2] Fremy, *Liebig's Annal.*, 1840 (36), 44.

[3] Maskelyne, *Journ. f. prakt. Chem.*, 1855 (65), 287.

[4] Sthamer, *Liebig's Annal.*, 1842 (43), 335 ; Krafft, *Berichte*, 1888 (21), 2265 ; Hell and Jordanow, *ibid.*, 1891 (24), 938.

[5] Chittenden and Smith, *Amer. Chem. Journ.*, 1884 (6), 217.

[6] Heintz, *Journ. f. prakt. Chem.*, 1855 (66), 19.

[7] Brodie, *Liebig's Annal.*, 1849 (71), 151 ; Nafzger, *ibid.*, 1884 (224), 251.

[8] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1897, 390.

[9] *Journ. Chem. Soc.*, 1898, 633.

[10] *Rec. d. trav. chim. Pays-Bas*, 1898, 182 ; 316.

[11] *Analyst*, 1896, 323.

Hours.	Grms.
12	1·298-1·320
36	1·244
60	1·211
84	1·134
108	1·086
132	1·044
156	1·028

Kreiss and Hafner,[1] however, found that 100 c.c. of alcohol, containing 95 per cent by volume, retain in solution at 0° C. 0·56 grm. only.

The solubility of palmitic acid in alcohol of various strengths and at different temperatures has been ascertained by *Falciola*[2] as follows :—

Grms. in 100 *c.c.*

	40° C.	30° C.	20° C.	10° C.
Absolute Alcohol	31·9	..	9·2	2·8
75 per cent Alcohol	3·59	1·19	0·43	0·24
50 per cent Alcohol	0·31	0·12	0·09	0·05

100 parts of absolute alcohol dissolve, at 19·5° C., 9·32 parts only.

R. F. Ruttan[3] ascertained the following solubilities in absolute alcohol :—

100 Grms. of Absolute Alcohol dissolve	
at ° C.	Grms.
0	1·45
5	2·0
10	4·0
15	6·5
20	9·9
25	16·8
28	29·0
36	81·0

In boiling alcohol palmitic acid dissolves very readily; therefore alcohol is conveniently used for purifying the acid. Petroleum ether does not dissolve it very readily.

Palmitic acid dissolves in concentrated sulphuric acid; on diluting this solution with water, palmitic acid separates unchanged. Boiling concentrated nitric acid attacks it very slowly. On oxidation in alkaline solution with potassium permanganate, acetic, butyric, caproic, oxalic, succinic, and adipic acids, as also acids having the composition $C_5H_9O_3$ and $C_{16}H_{32}O_4$ are formed. Concentrated solutions of permanganate yield lower members of the fatty acid series than do dilute solutions.

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[1] *Berichte*, 1903, 2769.

[2] *Gazz. chim.*, 1910 (40), 217.

[3] *Eighth International Congress of Applied Chemistry*, vol. 25, p. 341.

The metallic salts of palmitic acid resemble closely those of stearic acid (see p. 165), but they are somewhat more soluble. The behaviour of *sodium palmitate* with water has been described above (p. 127). 100 c.c. of 95 per cent alcohol dissolve 1·136 grms. of *potassium palmitate* at 22° C. (*Geitel and v. d. Want*[1]). *Lithium palmitate*[2] crystallises from hot alcohol in small white shining scales. 100 c.c. of water dissolve at 18° C. 0·011 grm., and at 25° C. 0·018 grm. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·0796 grm., and at 25° C. 0·0955 grm. The solubilities of the *ammonium salt* in alcohol, ether, and acetone have been given above (p. 140). *Silver palmitate* can be obtained in a crystalline form by adding an alcoholic solution of silver nitrate to an alcoholic solution of ammonium palmitate; silver palmitate separates from the solution in the shape of small, lustrous laminæ. *Lead palmitate* is almost insoluble in absolute ether and petroleum ether; 50 c.c. of the former dissolve 0·0092 grm. of the lead salt (cp. p. 142).

Copper palmitate forms a fine blue powder, melting above 100° C. without (apparent) decomposition. On boiling a toluene solution of this palmitate for two hours with lead, copper is precipitated.[3]

The solubilities in absolute alcohol of other palmitates are given in the following table:—

100 Parts of Absolute Alcohol dissolve		
	at 20° C.	at boiling point.
Calcium palmitate	0·0103 parts	...
Barium palmitate	0·0035 ,,	0·0128 parts
Magnesium palmitate	0·0146 ,,	0·0197 ,,
	at 19° C.	
Lead palmitate	0·0007 ,,	...
	at 21° C.	
Lead palmitate, freshly precipitated	0·0033 ,,	...

The quantitative determination of palmitic acid in palmitates is effected by decomposing their solutions with hydrochloric acid, washing the separated acid with water, dissolving it in (absolute alcohol or) ether, evaporating the solution to dryness, and finally drying in a desiccator over sulphuric acid. The acid cannot be determined with accuracy by weighing its calcium or barium salt (cp. p. 141).

Methylester, boils at 196° C. under 15 mm. pressure (*Haller and Youssoufian*); melting point 28° C. (*Berthelot*).

Ethylester, boiling point *in vacuo*: 122° or 138° C., according as to whether the vapours have to rise 25 mm. or 65 mm. (*Krafft*[4]); under 10 mm. pressure the ester boils at 184·5°-185·5° C. without decomposition (*Holzmann*[5]); melting point 24·2° C. (*Heintz*).

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[1] For the use of potassium palmitate in water analysis, cp. Blacher, Grünberg, and Kissa, *Chem. Zeit.*, 1913, 56.

[2] Partheil and Ferié, *Arch. d. Pharm.*, 1903, 545.

[3] Cp. Kahlenberg, *Journ. phys. Chem.*, 1902 (6), 6; C. B. Gates, *ibid.*, 1911 (15), 101.

[4] *Berichte*, 1903, 4340.

[5] *Arch. d. Pharm.* 236, 440.

Daturic Acid, $C_{17}H_{34}O_2$

In the older literature on fatty acids "margaric acid" of the formula $C_{17}H_{34}O_2$ was described and considered to represent a chemical individual. (The term "margarine" given to butter substitutes has been derived from "margaric" acid.) *Heintz*,[1] however, found that "margaric" acid represented that mixture of palmitic and stearic acids which has been described above as a eutectic mixture.

An acid of the formula $C_{17}H_{34}O_2$ which he found in Datura oil was described by *Gérard*[2] as daturic acid. *Holde*[3] also claimed to have found this acid. Later on, however, he showed[4] that this daturic acid represented a mixture of several acids. The same was thought to hold good of a heptadecyclic acid, which *Nördlinger*[5] stated to occur, to the extent of 1 per cent, amongst the solid fatty acids of palm oil. This acid melted at 57° C. and boiled between 223° and 225° C. under a pressure of 15 mm.; its magnesium salt crystallised in microscopic needles, melting at 135°-140° C. *Holde* claimed that this acid is a mixture of several solid acids, from which an acid of the melting point of 68°-68·5° and molecular weight 288 was isolated. *Kreis and Hafner*[6] stated to have found a heptadecylic acid in lard. *Bömer*,[7] however, proved that lard contains no heptadecylic acid.

A heptadecylic acid of the formula $C_{17}H_{34}O_2$ was prepared synthetically by *Krafft*, and the name "margaric acid" was assigned to it. This acid melts at 59·3° C. and boils under a pressure of 100 mm. at 227° C.[8]

This synthetical margaric acid was considered, in the light of the above-stated investigations to differ from the acid described by *Gérard*, until *H. Meyer and A. Eckert*[9] claimed to have found in coffeeberry oil one to one and a half per cent of an acid having the formula $C_{17}H_{34}O_2$, and melting at 57° C., the magnesium salt of which melted at 137°-142° C. and the methylester at 30° C.

Recently *Meyer and Beer*[10] isolated, from datura oil itself, a heptadecylic acid which they found to be identical with *Krafft's* synthetical margaric acid. Therefore the existence of daturic acid must be taken as proved.

Daturic acid melts at 59·5° C.; it dissolves more easily in alcohol than palmitic acid. The melting point of mixtures of palmitic and daturic acids has been given above. It would appear from the table given there, that the earlier observers had to deal with mixtures of daturic and palmitic acids. In order to prove the identity of daturic acid with synthetical margaric acid, *Meyer and Beer* examined the melting points of mixtures of synthetical margaric acid and palmitic acid. Their observations are reproduced in the following table:—

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[1] *Journ. f. prakt. Chem.*, 1855 (66), 1; *Poggend. Annal.*, 1852 (87), 553.

[2] *Compt. rend.*, 1890 (111), 305; *Annal. de Chim. et de Phys.*, 1892 (6), 27, 549.

[3] *Mitt. d. Königl. Techn. Versuchsanst.*, 1902, 66.

[4] *Berichte*, 1905 (38), 1247.

[5] *Zeits. f. angew. Chem.*, 1892, 110.

[6] *Berichte*, 1903, 2770; 1905, 1251.

[7] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1913 (23), 642.

[8] Cp. also *Le Sueur*, *Journ. Chem. Soc.*, 1904, 827; 1905, 1891.

[9] *Monatsh. f. Chem.*, 1910 (31), 1238.

[10] *Kaiserl. Akad. d. Wissenschaften, Wien*, January, 1912.

Margaric Acid. Per cent.	Palmitic Acid. Per cent.	Melting point. ° C.
100	0	59·5
83·7	16·3	55 -56
72·0	28·0	54·5-56
63·1	36·9	54·5-55·5
50·0	50·0	56 -57·5
30·8	69·2	58·5-59·5
20·0	80·0	59·5-60
0	100	62

It will be seen that this table is practically identical with the one given above.

Bömer and Limprich[1] recently prepared synthetical heptadecylic acid by *Krafft's* method, and found it to agree fully, in all its properties, with the daturic acid and the synthetical margaric acid described above. 100 c.c. of absolute alcohol dissolve at 0° 1·15 grms., and at 15° C. 3·48 grms.

A "margaric acid" was also prepared from cetyl iodide, using *Grignard's* reaction (cp. Vol. III. p. 1) by *R. F. Ruttan.*[2] This margaric is identical with the above-described margaric acid, for it melted at 59·9°-60° C. and solidified at 58·8° C.; $d^{60} = 0·8532$; $n_{D}^{60} = 1·4342$. Boiling point, under 100 mm. pressure 227° C. 100 grms. of absolute alcohol dissolve at 0° C. 1·53 grms., at 5·4° C. 2·42 grms., at 10° C. 4·12 grms., at 15° C. 6·72 grms., at 21° C. 13·4 grms., and at 28° C. 32·14 grms.

Ammonium margarate crystallises in light feathery transparent crosses.

Silver margarate is obtained from the ammonium salt by precipitation (in the dark) with silver nitrate in the form of fine white, striated prisms.

The *calcium, barium, magnesium,* and *lead* salts are insoluble in water and undergo partial hydrolysis.

Zinc margarate crystallises from boiling benzene in microscopic spheres and melts at 126·6° C.

Methylester, melts at 30° C.

Ethylester, melts at 26·7° C. (*Bömer and Limprich*); 27·5° C. (*Ruttan*).

STEARIC ACID,[3] $C_{18}H_{36}O_2$

Stearic acid occurs abundantly in many vegetable and animal fats, especially in the hard ones, such as cacao butter, shea butter, and tallow. In smaller quantities stearic acid is found in some waxes, such as wool wax, and most likely in spermaceti. The higher the melting point of a fat the higher is, as a rule, the proportion of stearic acid it contains. Stearic acid can be obtained synthetically by the reduction of unsaturated acids containing an open chain of 18 carbon atoms (oleic, linolic, linolenic, clupanodonic, also stearolic) by means of hydrogen in the presence of a suitable catalyst, such as nickel or palladium. (With regard to chaulmoogric acid, see p. 205.)

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (23), 641.

[2] *Eighth International Congress of Applied Chemistry*, vol. 25, p. 341.

[3] The existence of an isomeric stearic acid—isostearic acid $(C_4H_9)_2CH(CH_2)_5$-CH_2CHCH_3COOH—has been conjectured by Kunz-Krause and Massute.

Pure stearic acid forms white, nacreous laminæ melting at 69·32° C. to a perfectly colourless liquid which, on cooling, solidifies at 69·3° C. to a crystalline translucent mass. This melting point has been ascertained by *de Visser* for a very carefully purified specimen of acid (cp. p. 116 and p. 119). (*Saytzeff* gives the melting point 71°-71·5° C.; *Fritzweiler*, who prepared pure stearic acid from cacao butter oleodistearin, 70° C.) The acid boils under ordinary pressure at about 360° C. with slight decomposition; under a partial vacuum it distils, however, unchanged (*Chevreul*). Under 100 mm. pressure it boils at 291° C., under 15 mm. at 232° C., and *in vacuo* at 154·5°-155·5° C.[1] The acid may also be distilled in a current of superheated steam without undergoing destruction.

$d^{69\cdot2°}_{4°}$ C. = 0·8454; $d^{80°}_{4°}$ C. = 0·8386. At 11° C. the specific gravity of stearic acid equals that of water; at somewhat higher temperatures it floats on water, as it expands more quickly than the latter. $n^{80}_{D} = 1\cdot43003$, $n^{60}_{D} = 1\cdot4322$ (*Ruttan*).

Like palmitic acid stearic acid has neither smell nor taste; it is greasy to the touch, and produces a grease-spot on paper. It is insoluble in water. In hot alcohol it dissolves easily; it is less soluble in absolute alcohol than palmitic acid, one part of stearic acid requiring 40 parts of alcohol. 100 c.c. of alcohol (methylated), of specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume), were stated by *Hehner and Mitchell*[2] to dissolve at 0° C. 0·155 to 0·158 grm. after twelve hours' standing, and 0·145 to 0·153 grm. after thirty-six hours' standing. These numbers have been found to be too high by *Kreis and Hafner*, as also by *Emerson*.[3] *Kreis and Hafner* state that 100 c.c. of 95 per cent alcohol dissolve 0·1249 gram at 0° C. The numbers obtained by *Emerson*,[4] and set out in the following table, are in good agreement with *Kreis and Hafner's* observations:—

Solubility of Stearic Acid in Alcohol

Specific Gravity of Alcohol at 0° C.	Approximate Strength of Alcohol by Volume.	Amount of Stearic Acid dissolved in 100 c.c. at 0° C.
	Per cent.	Grm.
0·82650	95·7	0·1246
0·82715	95·5	0·1223
0·82871	95·1	0·1139
0·83126	94·5	0·1035
0·83183	94·3	0·0996

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[1] E. Fischer and C. Harries, *Berichte*, 1902, 2162, ascertained the boiling point 158°-160° under 0·25 mm. pressure (temperature of bath 190° C.).

[2] *Analyst*, 1896, 323.

[3] *Journ. Amer. Chem. Soc.*, 1907, 1751.

[4] *Chem. Revue*, 1905, 108.

The discrepancies are explained as being due to supersaturation, which, according to *Emerson*, does not take place if in the preparation of saturated solutions no less than 0·7 grm. for 100 c.c. of alcohol, or 0·5 for 50 c.c. of alcohol, are used.

The author is able in some measure to confirm these observations, for a solution of stearic acid prepared with 3 grms. per litre of alcohol of specific gravity 0·818 at 15·5° C. contained per 100 c.c. at 0° C. 0·0814 grm. of stearic acid, whereas when 7 grms. of stearic acid were used the solution was found to contain (in several preparations) 0·099, 0·1008, 0·1082, 0·0856, 0·0810, 0·0882 grm. per 100 c.c. of alcohol at 0° C. The solutions were allowed to stand in ice water over night, and after shaking in the morning remained in ice water for another half an hour before filtering. In one experiment, where the solution stood for three hours after shaking, 100 c.c. contained 0·0882 grm.

The solubility of stearic acid in alcohol of various strengths and at different temperatures has been ascertained by *Falciola*[1] as follows :—

Grms. in 100 *c.c.*

	40° C.	30° C.	20° C.	10° C.
Absolute Alcohol . . .	13·8	4·5	2·0	0·9
75 per cent Alcohol . .	0·77	0·39	..	0·15
50 per cent Alcohol . .	0·12	0·10	0·08	..

R. F. Ruttan[2] ascertained the following solubilities in absolute alcohol :—

100 Grms. of Absolute Alcohol dissolve	
at ° C.	Grms.
0	0·37
5	0·51
10	1·1
15	1·6
20	2·5
25	4·9
28	6·0
36	20·0

Stearic acid dissolves easily in ether; at 23° C. 1 part of benzene dissolves 0·22 part and 1 part of carbon bisulphide dissolves 0·3 part of the acid. Petroleum ether of specific gravity 0·672 dissolves at 0° C. only 0·4 per cent of stearic acid (*Charitschkoff*).

On oxidising stearic acid with potassium permanganate *Carette* obtained dibasic acids (succinic, adipic). *Marie*[3] found amongst the products of oxidation normal valeric acid (not isovaleric acid, contrary to previous statements[1]). By oxidation with hydrogen peroxide *Dakin* obtained quindecylmethylketone (cp. p. 144).

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[1] *Gazz. chim.*, 1910 (40), 217.

[2] *Eighth International Congress of Applied Chemistry*, vol. 25, p. 341.

[3] *Journ. Soc. Chem. Ind.*, 1896, 362.

On heating stearic acid with one-tenth of its weight of sifted cast-iron turnings to 280° C. stearone is formed (see p. 150).

Potassium stearate, $KC_{18}H_{35}O_2$, forms crystals having a greasy lustre; they dissolve in 6·6 parts of boiling alcohol. On diluting the hot aqueous solution with a large proportion of water, pearly laminæ of an acid stearate, $KC_{18}H_{35}O_2 . C_{18}H_{36}O_2$, separate. The salt is insoluble in ether, petroleum ether, carbon bisulphide, and chloroform. (Difference from potassium oleate.)

Sodium stearate, $NaC_{18}H_{35}O_2$, resembles closely the potassium salt. In the crystalline state it forms lustrous laminæ. The acid salt has the formula $NaC_{18}H_{35}O_2 . C_{18}H_{36}O_2$.

Lithium stearate,[2] $LiC_{18}H_{35}O_2$, crystallises from alcohol in small white scales. 100 c.c. of water dissolve at 18° C. 0·01 grm., and at 25° C. 0·012 grm. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·041 grm., and at 25° C. 0·0532 grm.

Ammonium stearate, $(NH_4)C_{18}H_{35}O_2$, loses part of its ammonia on being warmed in aqueous solution, and is converted into the acid salt. The same change takes place when the ammonia soap is allowed to stand in a desiccator over concentrated sulphuric acid. The solubilities of the ammonium salt in alcohol, ether, and acetone have been given above (p. 140).

Calcium, *strontium*, and *barium stearates* form crystalline precipitates, practically insoluble in alcohol. The *magnesium* salt crystallises in microscopical laminæ; it is nearly insoluble in cold alcohol, but sufficiently soluble in boiling alcohol to allow it to be crystallised from this menstruum.

Silver, *copper*, and *lead stearates* are amorphous.

The *lead* salt melts at 115°-116° C. without undergoing decomposition. It is very sparingly soluble in ether (difference from oleic acid), and less still in petroleum ether (*Twitchell*) (see above p. 141). 50 c.c. of absolute ether dissolve 0·0074 grm. of lead stearate (*Lidoff*). In hot benzene lead stearate dissolves, but separates almost completely on cooling to 8°-12° C. In absolute alcohol it is very sparingly soluble; it is, however, more soluble in this menstruum than is lead palmitate (*Salkowski*).

The insoluble salts of stearic acid are to some extent hydrolysed on washing with water. Thus barium stearate gives up to the water barium oxide, and free stearic acid (which can be extracted with alcohol) remains behind with the undissociated residue. This should be noted with regard to the quantitative determination of stearic acid (also of palmitic and oleic acids), as it has been proposed repeatedly to estimate stearic acid by weighing its calcium or barium salt.

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[1] The statement made by Fleurent (*Journ. Soc. Chem. Ind.*, 1898, 852), that stearic acid heated in thin layers at 120° C. with free admission of air is converted into an intermediate liquid form (in the cold) before definitely assuming the form of linoxyn, requires confirmation.

[2] Partheil and Ferié, *Arch. d. Pharm.*, 1903, 545.

Chittenden and Smith have shown that for accurate estimations the salts cannot be employed.[1] As pointed out above for palmitic acid, the free acid must be separated and weighed as such.

Methylester, boiling point, 214°-215° C.; melting point, 38° C. *Dreymann* proposes to use this ester as a substitute for cacao butter and spermaceti, and also as a basis for ointments.

Ethylester, boils *in vacuo* at 139° or 154° C., according to whether the vapours have to rise 25 mm. or 65 mm.;[2] it melts at 36·7° C.

Amylester, crystallises from hot alcohol in microscopic white plates, melting at 21° C.

Di-iodostearic acid, obtained by digesting ricinoleic acid with phosphorous iodide and hydriodic acid (see p. 218), is an oily viscous liquid. (*Chonowsky*[3]).

By treating this di-iodostearic acid with alcoholic potash an unsaturated acid is obtained which is isomeric with linolic acid. It differs from linolic acid in that it does not yield on oxidation with permanganate a tetrahydroxystearic acid, but resinous masses from which only azelaïc acid could be isolated. With regard to the action of zinc oxide on di-iodostearic acid, the original must be consulted.

With regard to the commercial preparation of stearic acid and its uses,[4] see Vol. III. Chap. XV.

ARACHIDIC ACID, $C_{20}H_{40}O_2$

Arachidic acid (discovered by *Gössmann*[5]) occurs in notable quantities in arachis oil,[6] in rambutan tallow (the fat from the seeds of *Nephelium lappaceum*, L.[7]), in smaller quantities in rape oil,[8] cacao butter,[9] macassar oil,[10] elderberry oil, nux vomica fat, Niam fat, and butter fat. It also occurs in the fat of dermoid cysts. It has been obtained synthetically from a fatty acid occurring in grape seed oil (erucic acid ?) by heating with melted caustic potash.[11]

Arachidic acid crystallises in small, lustrous scales, melting at 77° C. (*Baczewski*[12]). The acid is sparingly soluble in cold alcohol, but dissolves easily in boiling alcohol; if the boiling is prolonged, a small amount is converted into ethyl arachidate;[13] therefore, to avoid complications, the acid should only be boiled until it has just passed into solution. 100 parts of 90 per cent alcohol dissolve at 15° C. 0·022 parts, and at 20° C. 0·045 parts of arachidic acid. Arachidic acid dissolves readily in ether, chloroform, petroleum ether, and benzene.

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[1] Cp. also Pflüger, *Arch. f. Physiol.*, 1902 (89), 211; Fendler and Frank, *Zeits. f. angew. Chem.*, 1909, 256.

[2] Krafft, *Berichte*, 1903, 4340; cp. also Erdmann and Bedford, *Berichte*, 1909, 1327.

[3] *Berichte*, 1909, 3342.

[4] For the use of stearic acid in the separation of rare earths, see C. W. Stoddart and C. W. Hill, *Journ. Amer. Chem. Soc.*, 1911 (33), 1076.

[5] Heintz (*Poggendorff's Annalen*, 90, 146) described this acid as "Butinsäure" (butinic acid).

[6] Gössmann, *Liebig's Annal.*, 1854 (89), 1; Schweizer, *Arch. d. Pharm.*, 1884 (222), 757; Kreiling, *Berichte*, 1888 (21), 880.

[7] Ponzio, *Journ. f. prakt. Chem.*, 1893 (48), 487.

[8] See Vol. II. Chap. XIV. "Rape Oil."

[9] Traub, *Berichte*, 1883 (16), 1103.

[10] Thümmel and Kwasnik, *Arch. der Pharm.*, 1891 (229), 188.

[11] The statement made by Pickard and Yates (*Proc. Chem. Soc.*, 1903 (19), 147), that arachidic acid is obtained by the oxidation of cholesterol, must be rejected. Cp. Windaus, *Arch. d. Pharm.*, 1908, 117; cp. also *Journ. Chem. Soc.*, 1908, 1680.

[12] *Monatsh. f. Chem.*, 1896 (17), 530.

[13] This behaviour has not been observed in the case of palmitic and stearic acids.

The *potassium* salt of arachidic acid can be obtained from its alcoholic solution in crystals. The *copper* salt crystallises from alcohol in needles, the *silver* salt in prisms.

Methylester, melting point 54·5° C.

Ethylester, boiling point 284°-286° C. under 100 mm. pressure; melting point, 50° C.

Behenic Acid, $C_{22}H_{44}O_2$

Behenic acid occurs in ben (behen) oil from the seeds of *Moringa oleifera*.[1] It has also been found in the fat from dadap seeds,[2] and in the oil contained in Calabar beans.[3] It melts at 80°-82° C., solidifies at 79°-76° C.,[4] and boils under 60 mm. pressure at 306° C. Synthetical behenic acid from erucic acid[5] melts at 83°-84° C., and solidifies at 79°-77° C.

Behenic acid crystallises in needles; it is less soluble in alcohol than in ether. 100 parts of alcohol dissolve at 17° C. 0·102 grm., and 100 parts of ether at 16° C. 0·1922 grm. With regard to chloro- and bromo-derivatives of behenic acid, see *D. Warmbrunn*.[6]

Ethylester, melting point 48°-49° C. (*Voelcker*).

Lignoceric Acid, $C_{24}H_{48}O_2$

Lignoceric acid has been shown by *Kreiling*[7] to occur in arachis oil, in association with arachidic acid. Lignoceric acid melts at 80·5° C.; the melted acid solidifies on cooling to a mass showing radiated structure; on cooling it becomes brittle. The acid crystallises from alcohol in white flocks of silky lustre; these become scaly and show nacreous lustre when pressed between filter paper. Lignoceric acid is very sparingly soluble in cold alcohol, but dissolves readily in benzene, ether, and carbon bisulphide.

Lead lignocerate, insoluble in ether, sparingly soluble in absolute alcohol, but easily soluble in boiling benzene, melts at 117° C.

Copper lignocerate is very sparingly soluble in absolute alcohol and ether, but dissolves in hot benzene.

Methylester, melting point 56·5°-57° C.; is stated to distil without undergoing decomposition.

Ethylester, melting point 55° C.; distils without undergoing decomposition at 305°-310° C. under a pressure of 15-20 mm.

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[1] Voelcker, *Liebig's Annal.*, 1848 (64), 342. With regard to its occurrence in rape oil (Reimer and Will, *Berichte*, 1887 (20), 2389), cp. Vol. II. Chap. XIV. "Rape Oil."

[2] N. H. Cohen, *Chemisch Weekblad*, 1909, No. 41.

[3] Salway, *Journ. Chem. Soc.*, 1911, 2148.

[4] *Journ. f. prakt. Chem.*, 1894 (49), 61.

[5] Talanzeff, *ibid.*, 1895, (50); 71-73; cp. also de Wilde and Reychler, *Bull. Soc. Chim.*, 1889, 1, 296; Stohmann and Langbein, *Journ. f. prakt. Chem.*, 1890 (42), 328; Fileti and Ponzio, *Gazz. Chim.* 23, 392; 27, 298.

[6] *Inaug. Dissert.*, 1903, Königsberg.

[7] Kreiling, *Berichte*, 1888 (21), 880.

Carnaübic Acid, $C_{24}H_{48}O_2$

This isomeride of lignoceric acid, stated to occur as an ester (combined with higher alcohols[1]), in carnaüba wax, wool wax,[2] and coffee wax,[3] probably represents a mixture of several acids.[4] (Carnaübic acid is also stated to occur in "carnabon," a phosphatide isolated from the kidney (*E. K. Dunham and C. A. Jacobson*).[5] The author's doubt as to its individuality is all the more justified as a "carnaübyl alcohol" (from which carnaübic acid is stated to have been obtained by oxidation with chromic acid in glacial acetic acid solution) has been shown to consist of a mixture of melissyl alcohol and a hydrocarbon.[6] The following statements must therefore be accepted with reserve. The acid is sparingly soluble in cold methyl alcohol, but easily soluble in cold benzene, in boiling alcohol, ether, acetone, petroleum ether, and glacial acetic acid. It melts at 72·5° C. (*Stürcke*), 74° C. (*Meyer and Eckert*), and solidifies at 69°-67° C.

The *ammonium* salt is stated to be insoluble in cold water and alcohol, but soluble in the hot. The *potassium* salt is said to be sparingly soluble in water and in cold alcohol, and to dissolve more easily at higher temperatures. The *lithium* salt forms a white microcrystalline powder, melting at 215°-216° C. It is very sparingly soluble in water and in alcohol, even in the hot. The *lead* salt melts at 110°-111° C.; it is soluble in toluene.

Methylester, melting point 54°-55° C.

Ethylester, melting point 49°-50° C.

Pisangcerylic Acid, $C_{24}H_{48}O_2$

This isomeride of lignoceric acid is stated to occur as an ester of pisangceryl alcohol in pisang wax. Its melting point is given as 71° C. The existence of this acid would seem to require confirmation.

Hyænic Acid, $C_{25}H_{50}O_2$ (?)

The glyceride of this acid has been stated[7] to occur in the anal glandular pouches of the striped hyæna. The acid, which is stated to melt at 77°-78° C., is probably a mixture of several fatty acids. The *calcium salt* is stated to represent a crystalline powder, melting at 85°-90° C.

Cerotic Acid, $C_{26}H_{52}O_2$

Cerotic acid[8] occurs in the free state in beeswax (*Brodie*), in carnaüba wax (*Bérard*[9]), and in montan wax[10]). It has been shown to be present in insect (Chinese) wax,[1] opium wax,[2] and in wool wax,[3] in combination with ceryl alcohol, as ceryl cerotate. As a glyceride it is stated to occur in the fatty oil from *Aspidium filix mas*,[4] as also from other ferns.[5]

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[1] Stürcke, *Liebig's Annal.* 223, 306.

[2] *Journ. Soc. Chem. Ind.*, 1896, 460; *Berichte*, 29, 618; 2892; 31, 97.

[3] H. Meyer and A. Eckert, *Monatsh. f. Chem.*, 1910 (31), 1233.

[4] Röhmann, *Zentralb. f. Physiol.*, 1905, 317.

[5] *Zeits. phys. Chem.*, 1910 (64), 302.

[6] Matthes and Sander, *Arch. d. Pharm.*, 1907 (246), 169.

[7] Carius, *Liebig's Annal.*, 1864 (129), 168.

[8] The acid was discovered by John, who named it "cerin."

[9] *Zeits. f. Chem.*, 1868, 415.

[10] Th. Rigg, *Transact. New Zealand Inst.*, 1911 (64), 270.

Crude cerotic acid is obtained by exhausting beeswax with boiling alcohol. It is a wax-like mass, melting between 78° and 82° C. On cooling it separates from its alcoholic solution (in thin, straight or curved needles) so completely in the course of a few hours, that the addition of water to the filtrate produces only a milky turbidity but no precipitate. (Essential difference from palmitic and stearic acids.) *Marie*[6] states that the crystals deposited from alcohol vary according to the purity of the acid, but in the opinion of *H. Meyer and A. Eckert* the conclusions are vitiated by the employment of alcohol for recrystallisation. Pure cerotic acid crystallises from alcohol in stellate, microscopic needles, melting at 77·8° C. (corr.), from benzene in dense laminæ, and from ether in tabular masses consisting of large aggregated needles. (If the acid contains neutral substances, the crystals deposited from alcohol form a gelatinous mass consisting of microscopic needles, and containing a large proportion of alcohol; if the impurity is melissic acid, short granular crystals separate.) In *Rigg's*[7] opinion a cerotic acid which crystallises in needles must still be considered as impure, the criterion of purity being crystallisation in pearly scales (nacreous crystalline plates). $d\frac{79°}{4°}$ C. = 0·8359.

On boiling with sodium carbonate or dilute aqueous caustic soda, the acid does not pass into solution; it dissolves, however, in boiling alcoholic potash. On cooling, the potassium cerotate thus formed solidifies to a mucilaginous mass (*Barfoed*).

Cerotic acid can be estimated volumetrically in its alcoholic solution by titration with caustic potash, phenolphthalein being the indicator. By using this method[8] for the determination of the molecular weight (Chap. VIII.), the uncertainty which attached for a long time to the composition of cerotic acid has been definitely removed in favour of the formula $C_{26}H_{52}O_2$.

Schalfejeff[9] had thrown some doubts on the existence of an acid of the composition of cerotic acid; these doubts were, however, removed by *Nafzger*,[10] by *Zatzek*,[11] and by *Marie*.[12] Yet the ultimate composition of cerotic acid was not established with certainty by these chemists, as the elementary analyses of cerotic acid and its esters agreed with either of the formulæ $C_{26}H_{52}O_2$, or $C_{25}H_{50}O_2$.[13] No definite information can be gained from ultimate analysis as the differences in the percentage compositions approximate closely to the errors of the analytical method itself, as a glance at the following table will show:—

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[1] Brodie, *Liebig's Annal.*, 1848 (67), 199.

[2] O. Hesse, *Berichte*, 1870 (3), 637.

[3] Buisine, *Bull. Soc. Chim.*, 1884 (42), 201.

[4] Katz, *Arch. d. Pharm.*, 1898 (236), 660.

[5] Blasdale, *Journ. Amer. Chem. Soc.*, 1903 (25), 1151.

[6] *Ann. de Chim. et de Phys.*, 1896 (7), 145.

[7] Th. Rigg, *Transact. New Zealand Inst.*, 1911 (64), 270.

[8] Lewkowitsch, *Proc. Chem. Soc.*, 1890, 92.

[9] *Berichte*, 9, 278, 1688.

[10] *Liebig's Annal.* 224, 256.

[11] *Berichte*, 15, 2625.

[12] *Journ. Soc. Chem. Ind.*, 1894, 1207; 1895, 599.

[13] *Ibid.*, 1896, 362.

	C	H	O
	Per cent.	Per cent.	Per cent.
$C_{27}H_{54}O_2$.	79·02	13·17	7·81
$C_{26}H_{52}O_2$.	78·80	13·12	8·08
$C_{25}H_{50}O_2$.	78·53	13·09	8·38

In the case of the neutralisation values of the three acids, however, the differences are larger than the errors inherent to the method,[1] as the following table shows :—

	Molecular Weight.	Neutralisation Value.
$C_{27}H_{54}O_2$	410	136·8
$C_{26}H_{52}O_2$	396	141·7
$C_{25}H_{50}O_2$	382	146·8

Since *Lewkowitsch*[2] ascertained the neutralisation value of pure cerotic acid from beeswax to be 142·1, and *Henriques*,[3] later on, that of cerotic acid from Chinese wax to be 141·4, the formula $C_{26}H_{52}O_2$ must be accepted as representing the true composition of cerotic acid.

Sodium and *potassium cerotates* are easily soluble in boiling water.

Magnesium cerotate melts at 174°-176° C. A one per cent solution of pure cerotic acid in boiling alcohol gives no precipitate with magnesium acetate; after cooling to 50° C. the salt separates out. However, if the cerotic acid contain melissic acid, an immediate precipitate is obtained.

Lead cerotate is insoluble in water, alcohol, and ether. It dissolves in hot benzene and crystallises from this solution in needles melting at 112·5°-113·5° C.

Methylester melts at 60° C. (*Nafzger*), 62° C. (*Marie*); the ester distils *in vacuo* without undergoing decomposition. In the cold it is sparingly soluble in petroleum ether, methyl, and ethyl alcohol, but easily soluble in the hot. It is also easily soluble in ether, benzene and chloroform.[4]

Ethylester, crystallises from alcohol in fine needles melting at 59°-60° C.; 58·5°-59° C. (*Rigg*). The ester distils *in vacuo* without undergoing decomposition; under a pressure of 14 mm. at 285° C. (*Rigg*); by distillation under atmospheric pressure it is broken up into cerotic acid, ethylene, carbonic dioxide, a hydrocarbon $C_{26}H_{54}$, and the ketone $C_{53}H_{106}O$.

Cerylester, see Chap. I. (p. 65).

MONTANIC ACID, $C_{28}H_{56}O_2$

Montanic acid occurs in distilled montan wax, and was considered to be the acidic portion of a wax contained in the bitumen extracted from lignite (by means of volatile solvents) (Vol. III. Chap. XV. "Montan Wax"). Recently *Rigg*[1] has shown that what hitherto has been considered as montanic acid (having the formula $C_{29}H_{58}O_2$) represents in reality a mixture of cerotic, montanic, and melissic acids.

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[1] *Proc. Chem. Soc.*, 1890, 92. [2] Cp. *Jahrb. d. Chemie*, 1897 (7), 369.

[3] *Zeits. f. ang. Chem.*, 1897, 366.

[4] Lipp and Kuhn, *Journ. f. prakt. Chem.*, 1911 (86), 92.

Pure montanic acid crystallises from acetic acid in colourless plates (pearly scales), melting at 83° C. (Crude montanic acid crystallises in needles.) It is soluble in hot alcohol and glacial acetic acid, but much more soluble in petroleum ether and ethyl acetate; it is only slightly soluble in methyl alcohol (whereas cerotic acid is easily soluble and melissic acid is insoluble in this solvent).

Methylester, melts at 67°-67·5° C. (*Rigg*), 66° C. (*H. Ryan and J. Algar*[2]).

Ethylester, melts at 67° C. (*Rigg*), 64-65° C. (*H. Ryan and J. Algar*).

The *amide*, *anilide*, and *ketone* have been mentioned above (see p. 148).

MELISSIC ACID, $C_{30}H_{60}O_2$

Melissic acid occurs in the free state in beeswax.[3] Recently, it has been found (*Rigg*[1]) to form a constituent of montan wax. It crystallises in scales possessing silky lustre, and melting at 91° C. *Schwalb*[4] prepared from beeswax melissyl (myricyl) alcohol, a melissic acid crystallising from petroleum ether in small, fine needles, and melting at 88·5°-89° C. To this acid he ascribes the formula $C_{31}H_{62}O_2$. The melissic acid of the formula $C_{30}H_{60}O_2$, obtained by *Brodie*,[5] from melissyl alcohol by heating with potash lime (see Chap. IX.) is more likely to represent true melissic acid. This acid is readily soluble in warm alcohol, chloroform, carbon bisulphide, and petroleum ether, and sparingly soluble in ether and methyl alcohol. Melissic acid obtained by *Matthes and Sander* by oxidising melissyl alcohol from laurel oil (see Vol. II. Chap. XIV. "Laurel Oil") melts at 91° C. It appears very likely that the acid prepared by *Schwalb* is identical with the acid $C_{30}H_{60}O_2$. The melissic acid found by *Rigg* to be a constituent of montan wax crystallises in pearly scales, melting at 88·5° C.

Magnesium melissate forms a white powder insoluble in alcohol, ether, and petroleum ether, soluble in hot chloroform, toluene, and benzene. From its solution in benzene it separates in the form of a jelly. In a capillary tube it conglutinates at 150° C., and melts at 160° C. to a viscous transparent liquid, solidifying on cooling to a vitreous mass (*Schwalb*[6]).

Silver melissate, prepared by dissolving melissic acid in 100 parts of alcohol, and adding a small excess of an alcoholic solution of silver nitrate, separates on cooling as an amorphous white powder. In a capillary tube it conglutinates at 94° C., and turns black at 140° C.

Lead melissate is insoluble in alcohol and ether, soluble in boiling chloroform. It crystallises from toluene in needles melting at 118°-119° C. (*Stürcke* [1]).

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[1] *Transact. New Zealand Inst.*, 1911 (64), 270.

[2] *Proc. Roy. Irish Acad.*, 1913, 97.

[3] Nafzger, *Liebig's Annal.*, 1884 (224), 249; Marie, *Ann. de Chim. et de Phys.*, 1896 (7), 198.

[4] *Liebig's Annal.* 235, 135.

[5] *Ibid.* 71, 149.

[6] Cp. also Matthes and Sander, *Arch. d. Pharm.* 246, 172.

Methylester, melting point 74·5° C. (*Marie*).

Ethylester, melting point 73° C. (*Pieverling* [2]).

Myricylester (see Chap. I. p. 66).

PSYLLOSTEARYLIC ACID, $C_{33}H_{66}O_2$

This acid is stated to occur in Psylla wax combined with psyllostearylic alcohol.[3] It is easily soluble in alcohol, less soluble in petroleum ether and in common ether. The crystallised acid melts at 94°-95° C. The formula given by *Sundwick* would seem to require confirmation.

II.—ACIDS OF THE OLEIC SERIES, $C_nH_{2n-2}O_2$

The naturally occurring acids belonging to the oleic (or acrylic series; from acrylic acid, its lowest member) are unsaturated compounds, and are therefore capable of absorbing hydrogen, chlorine, bromine, iodine, and the hydrogen acids of the halogens. Thus they can be converted into acids or derivatives of acids of the acetic series. It should be noted that, whereas halogens and their hydrogen acids are readily assimilated, *hydrogen* is not taken up by the higher members of this series when they are acted upon with sodium amalgam in alkaline solution, or with nascent hydrogen—evolved by any other method—under pressure. They assimilate *hydrogen* only when the latter acts in the presence of a catalyst. Under suitable conditions complete reduction to a saturated acid takes place. Reduction of the unsaturated acid with the aid of hydrogen also occurs under the influence of silent electrical discharges. In the latter event, however, the reduction does not reach completion. Nor is complete reduction obtained by heating with phosphorus and fuming hydriodic acid under pressure at temperatures at which formation of hydrocarbons does not take place. Ozone is easily assimilated with the formation of ozonides and perozonides (see "Oleic Acid," p. 183).

The lower members of this series are miscible with water in every proportion. With the increase of the number of carbon atoms the solubility in water decreases. The specific gravities also decrease. The lower members can be distilled without undergoing decomposition; but the higher acids cannot be so distilled under ordinary pressure. However, in a current of superheated steam or *in vacuo* they pass over unchanged (cp. p. 119).

The unsaturated acids are more readily soluble in alcohol than the saturated acids having the same number of carbon atoms.

Some of the higher acids, notably oleic and erucic acids, are changed into crystallisable isomerides when treated with a small quantity of nitrous acid at the ordinary temperature, or with sulphurous acid or bisulphites at high temperatures and under pressure. Under certain conditions of catalytic reduction with hydrogen, especially with copper as the catalyst, oleic acid is converted into a solid isomeride (*Lewkowitsch*[1]).

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[1] *Liebig's Annal.* 223, 298.

[2] *Ibid.* 183, 355.

[3] Sundwick, *Zeits. f. physiol. Chem.*, 1901 (32), 355.

By oxidation with a dilute solution of potassium permanganate in alkaline solution, the unsaturated acids are converted into the corresponding hydroxylated acids (see p. 224).

When melted with caustic alkalis they are broken up into two lower acids; thus oleic acid yields palmitic[2] and acetic acids (cp., however, p. 158). The opinion held previously, that the cleavage occurs at the place which the doubly linked carbon atoms occupy, must be abandoned (see "Constitutional Formula of Oleic Acid"), and for it must be substituted the view that during the reaction a migration of the double-linkage takes place. This is also evidenced by the fact that petroselinic acid also yields acetic and palmitic acids with melted caustic potash.

According to the position of the doubly linked carbon atoms in the molecule of the higher acids of this series, a considerable number of isomerides, apart from geometrical isomerides (such as elaïdic and brassidic acids), is theoretically possible (see below). In this treatise, acids which do not occur in nature are left out of detailed consideration, hence such isomeric oleic acids as α-β oleic acid can only be referred to in passing. It should, however, be pointed out that recently *Ponzio and Gastaldi*[3] have shown that whereas ordinary oleic acid absorbs the theoretical amount of iodine, 2,3 oleic acid, which has the double linking between the α and β carbon atoms, absorbs under the ordinary conditions of the iodine absorption test (see Chap. VI.) only 3 to 18 per cent of iodine (as against the theoretical 90 per cent). Only by prolonged action of the *Wijs'* iodine solution, numbers approaching the theoretical values were obtained.

It must, however, be distinctly understood that it would be altogether premature to generalise from this observation, all the more so as petroselinic acid, which is a 6,7 oleic acid, absorbs readily the theoretical amount of iodine in *Hübl's* test.

Hitherto four isomeric acids of the composition $C_{16}H_{30}O_2$, as also five isomeric "oleic" acids, have been found to occur in nature. Moreover, indications have been obtained as to the existence of several other "oleic" acids in commercial products of the fat and oil industries. The acids of the composition $C_{22}H_{42}O_2$, to which erucic acid belongs, simulate oleic acid completely.

For the determination of the chemical constitution of the higher acids, that is to say, for the determination of the position of the doubly linked carbon atoms within the molecule, the following three methods have hitherto been employed :—

(1) *Conversion of the unsaturated acids into acids of the "stearolic series"* (see p. 234) by heating the dibromides of the saturated acids

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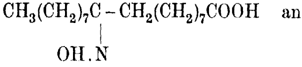
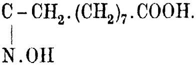
[1] Unpublished observation.

[2] Varentrapp, *Liebig's Annal.*, 1840 (35), 209.

[3] *Gazz. chim. ital.*, 1912 (42), 98.

with alcoholic potash under pressure. Taking, as an example, ordinary oleic acid, $CH_3.(CH_2)_7.CH=CH(CH_2)_7.COOH$, its dibromide yields a stearolic acid of the formula $CH_3(CH_2)_7C\equiv C(CH_2)_7COOH$. By treatment with concentrated sulphuric acid this stearolic acid is converted into the keto-acid: $CH_3.(CH_2)_7CO-CH_2.(CH_2)_7.COOH$, which furnishes with hydroxylamine hydrochloride two stereo-isomeric oximes, viz.:  $CH_3(CH_2)_7\underset{\overset{\mid}{OH.N}}{C}-CH_2(CH_2)_7COOH$ and $CH_3.(CH_2)_7.$  $\underset{\overset{\mid}{N.OH}}{C}-CH_2.(CH_2)_7.COOH$. These, in their turn, are converted by concentrated sulphuric acid into the two amino-acids: $CH_3(CH_2)_7.NH.CO.CH_2(CH_2)_7.COOH$ and $CH_3.(CH_2)_7.CO.NH.CH_2(CH_2)_7COOH$. On heating the latter with concentrated hydrochloric acid, nonylic and azelaïc acids are obtained, wherefrom the conclusion may be drawn that the double bond in ordinary oleic acid is to be found between the ninth and tenth carbon atom of the chain.

(2) *Conversion of the unsaturated acids into their ozonides.*—For the preparation of the ozonides[1] a weighed quantity of unsaturated fatty acids is dissolved in hexane, and a current of ozonised air (which need not contain more than 2 per cent of ozone) is passed through the solution at a temperature of $-20°$ C., until no more ozone is absorbed. The solvent is then evaporated off *in vacuo*, at a temperature not exceeding 30° C., until the weight remains constant. The increase in weight over the original fatty acid furnishes the amount of ozone absorbed by the fatty acid. If chloroform be used as a solvent perozonides are obtained (cp. p. 183).

On boiling the ozonides with water or alkali or glacial acetic acid, they are split into aldehydes of a saturated acid and semi-aldehydes of dibasic acids. Thus, oleic acid ozonide yields nonyl aldehyde and the semi-aldehyde of azelaïc acid. The conclusion may be drawn, therefrom, that the double linkage in oleic acid occurs between the ninth and tenth carbon atom. It must, however, be pointed out that the assumption is made here that the aldehydes formed are primary decomposition products; for the possibility must not be lost sight of that at first labile aldehydes or aldehydo-acids may be formed which are further decomposed with the formation of lower aldehydes (cp. "Oleic Acid," p. 184, "Elæostearic Acid," p. 201, and "Linolenic Acid," p. 206).

(3) *Conversion of unsaturated fatty acids into nitrogen tetroxide addition products.*[2]—The nitrogen tetroxide addition products are prepared by dissolving the unsaturated fatty acids in 5 to 6 volumes of petroleum ether and cooling in ice. In case the substance separates out, the liquid is well stirred, so that separation in the form of very minute crystals takes place, which do not influence unfavourably the progress

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[1] Harries and Türk, *Berichte*, 1906, 2844; 3667; cp. also Erdmann, *Berichte*, 1909, 1334.

[2] Jegorow, *Journ. f. prakt. Chem.*, 1912 (86), 521. The method was first published in *Journ. Russ. Phys. Chem. Soc.*, 1903 (35), 716.

of the reaction. As soon as the solution has cooled to 3°-4° C., the dry liquid nitrogen tetroxide (kept in sealed glass tubes) is added in a quantity slightly exceeding the theoretical quantity. The tetroxide is best previously dissolved in petroleum ether cooled in ice, and the solution is added in small quantities to the petroleum ether solution of the unsaturated substances. Immediately after adding the first portion, as a rule, no reaction takes place, but after a short time the temperature rises, so that subsequent portions must not be added, before the temperature falls again to 5°-6° C.; otherwise the petroleum ether begins to boil and the contents of the flask may become spontaneously ignited. After the whole amount of tetroxide has been added, the product is kept in ice overnight, and the addition product, generally representing a viscous oil, is drawn off by means of a pipette and heated in a sealed tube with 3 to 4 volumes of fuming hydrochloric acid at 130°-140° for 3 to 5 hours.

The information furnished by this method is of the same order as that obtained by the ozonide method. Thus, *oleic acid* yielded pelargonic acid and azelaïc acid; *isoöleic acid* (of the m.p. 42° C.) yielded caprylic and sebacic acids; *erucic acid* gave nonylic (nonoic) and brassylic acids. Hence, the following structural formulæ are derived: Oleic acid, $CH_3.(CH_2)_7.CH=CH(CH_2)_7COOH$; isoöleic acid, $CH_3.(CH_2)_6CH=CH(CH_2)_8COOH$; erucic acid, $CH_3(CH_2)_7CH=CH(CH_2)_{11}COOH$. (With regard to ricinoleic acid, see below, p. 215.)

The method of oxidising the unsaturated acids with alkaline potassium permanganate and identifying the oxidation products cannot be relied upon as a safe means for determining the position of the double bond. In those cases, where no dihydroxy acid of the same number of carbon atoms is formed, but acids with a lower number of carbon atoms result, no certainty obtains, as to whether the cleavage takes place at the double linking or whether, previously, migration thereof occurs, as is the case on treating unsaturated fatty acids with melted caustic potash. Nevertheless there is a justifiable presumption in assuming that the cleavage does occur at the position of the double linkage. Thus oleic acid, the constitution of which may be accepted as fairly well established (see below), yields (in addition to dihydroxy stearic acid) azelaïc and pelargonic acids, although the latter in small quantity only. The formation of these two acids would seem to confirm the position of the double linkage in the middle of the molecule, but it must not be overlooked that a considerable proportion of oxalic acid is formed; whence the conclusion might be drawn that ordinary oleic acid is a mixture of 9,10 oleic and 2,3 oleic acids (cp. p. 178, footnote 3).

By the action of concentrated sulphuric acid or anhydrous zinc chloride, oleic, elaïdic, and "isoöleic" acids yield γ-stearolactone. Erucic acid leads thus to behenolactone (and κ-λ undecylic acid yields undecolactone). Crotonic and α-hydroxybutyric acids, however, do not give rise to the formation of lactones.[1]

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[1] Shukoff and Schestakoff, *Journ. Russ. Phys. Chem. Soc.*, 1908 (40), 830.

A characteristic property of the lead salts of the higher acids of this series is their solubility in ether; this property is made use of in the separation of the higher acids of this series from the corresponding saturated acids. Elaïdic acid, however, simulates stearic acid as regards the solubility of its lead salts in ether (cp. p. 141); lead "isooleate" is less readily soluble in ether than is the oleate; the lead salt of erucic acid is sparingly soluble in cold ether.

The interaction of unsaturated acids (oleic) with mercury acetate in acetic acid was studied by *A. Leys.*[1]

For a preliminary note on the interaction of oleic and elaïdic acids with formaldehyde, the reader must be referred to the original paper by *S. Fokin.*[2]

Tiglic Acid, $C_5H_8O_2 = CH_3.CH:C(CH_3).COOH$

Tiglic acid (isomeric with angelic acid) occurs in croton oil. The acid crystallises in triclinic columns melting at 64·5° C. and boiling at 198·5° C. under ordinary pressure. $d^{76} = 0{\cdot}9641$.

Fittig's[3] researches proved that tiglic acid occurs as such in croton oil, and is not formed from angelic acid under the influence of the caustic soda used in saponifying the oil (as has been assumed repeatedly), for on prolonged boiling of angelic acid with caustic soda hardly 5 per cent of tiglic acid was obtained.

On melting tiglic acid with caustic potash, acetic and propionic acids are produced. By oxidation with potassium permanganate, carbonic acid, acetaldehyde, acetic acid, and dihydroxytiglic (tigliceric) acid are formed.

The *calcium* salt, $Ca(C_5H_7O_2)_2 + 3H_2O$, is more readily soluble in boiling water than that of angelic acid. 100 parts of water dissolve at 17° C. 6·05 parts of the anhydrous salt.

Ethylester boils at 156° C.

Acids $C_{12}H_{22}O_2$ and $C_{14}H_{26}O_2$

These acids are said to occur in the fat of cochineal.[4]

Acids $C_{16}H_{30}O_2$

(*a*) Hypogæic Acid, $C_{16}H_{30}O_2$

This acid was stated by *Gössmann and Scheven*,[5] and by *Schröder*[6] to occur in arachis oil. *Schoen*,[7] however, could not detect hypogæic acid in this oil, and although his statement is confirmed by *Bodenstein*,[8] yet the hypogæic acid prepared by the latter synthetically from stearolic acid, and having the constitutional formula $CH_3(CH_2)_7.CH=CH(CH_2)_5$ COOH, exhibits the properties of the acid obtained by *Schröder* from arachis oil. The acid is also stated to occur in maize oil.

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[1] *Bull. Soc. Chim.* iv. (1907), 343.

[2] *Journ. Russ. Phys. Chem. Soc.*, 1911 (43), 809.

[3] *Liebig's Annal.* 283, 65. Cp. also Rupe, Ronus, and Lotz, *Berichte*, 1902, 4265.

[4] Raymann, *Monatsh. f. Chem.*, 1885 (6), 895. According to Ljubarsky the acid from the fat of *Coccus axin* (Mexico) has the composition $C_{16}H_{30}O_2$ (physetoleic ?).

[5] *Liebig's Annal.*, 1855 (94), 230; Caldwell and Gössmann, *ibid.*, 1856 (99), 305.

[6] *Liebig's Annal.*, 1867 (143), 22.

[7] *Ibid.*, 1888, 244, 253.

[8] *Berichte*, 1894, 3397. Cp. also Marasse, *ibid.*, 1869, 359.

Hypogæic acid[1] crystallises in needles melting at 33°-34° C., boiling at 236° C. under a pressure of 15 mm., and at 230° C. under a pressure of 10 mm. It absorbs two atoms of bromine to form hypogæic dibromide (dibromopalmitic acid), an amorphous mass melting at 29° C. (*Schröder*[2]).

Hypogæic dibromide yields on treatment with silver oxide dihydroxypalmitic acid (see below). Boiling alcoholic potash converts it into palmitolic acid.

Gaïdic Acid, $C_{16}H_{30}O_2$. On passing nitrous acid fumes through hypogæic acid, its stereo-metrical isomeride, *gaïdic acid,* is obtained. Gaïdic acid melts at 39° C. (*Caldwell and Gössmann*[3]).

(*b*) PHYSETOLEIC ACID, $C_{16}H_{30}O_2$

Physetoleic acid is said to occur in Caspian seal oil[4] and in sperm oil.[5] The acid differs from hypogæic acid in that it is not transformed into a stereometrical isomeride by nitrous acid, and from palmitoleic acid by yielding a dihydroxylated acid which differs from that obtained from palmitoleic acid. Physetoleic acid is stated to melt at 30° C. On dry distillation it does not yield sebacic acid.

(*c*) PALMITOLEIC ACID,[6] $C_{16}H_{30}O_2$

This acid is stated by *Bull*[7] to occur in cod liver oil and to form about 6 per cent of the total fatty acids. It was isolated by converting the cod liver oil glycerides into their methyl esters, fractionating the mixed esters under a pressure of 10 mm., and freeing the fraction boiling at 185°-186° C. from methyl palmitate. The ester of palmitoleic acid was then converted into the barium salt, the latter recrystallised from ether, the acid isolated from the salt, and finally purified by means of its zinc salt. The acid is stated to solidify at $-1{\cdot}5°$ C.

A means of identifying this acid would be furnished by catalytic reduction with hydrogen, when palmitic acid should be obtained (*Lewkowitsch*).

On oxidising the acid at 0° C. with an alkaline solution of potassium permanganate, a dihydroxypalmitic acid of the melting point 125° C. was obtained; this acid appears to differ from the dihydroxystearic acid obtained by *Ljubarsky* from Caspian seal oil.

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[1] A hypogæic acid having the structure $CH_3(CH_2)_{12}.CH=CH.COOH$ was prepared from a bromopalmitic acid by Ponzio (*Gazz. chim. ital.*, 1905 (35), ii. 132.

[2] *Liebig's Annal.*, 1867 (143), 24.

[3] *Liebig's Annal.*, 1856 (99), 307.

[4] Ljubarsky, *Journ. f. prakt. Chem.*, 1898 (57), 26.

[5] Hofstädter, *Liebig's Annal.*, 1854 (91), 177.

[6] Bull had not named this acid; the author proposed, therefore, the name palmitoleic acid. Cp. *Jahrbuch d. Chem.*, 1906, xvi. 402. This acid must not be confounded with palmitolic acid.

[7] *Berichte*, 1906, 3574.

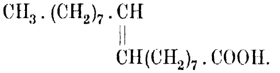
(*d*) Lycopodic Acid, $C_{16}H_{30}O_2$

This acid is stated to occur in the spores of lycopodium[1] as a glyceride, and to form 81 per cent of the mixed fatty acids of lycopodium oil (*Rathje*[1]). It differs from the acids described under (*a*) and (*b*) by being liquid at the ordinary temperature. Potassium permanganate oxidises it to dihydroxypalmitic, isocaproic, and hydroxycapric acids. Melting caustic potash decomposes it to isobutyric and lauric acids. Lycopodic acid does not, therefore, appear to have a normal structure.

Acids, $C_{18}H_{34}O_2$

An extremely large number of isomeric acids having the formula $C_{18}H_{34}O_2$ may exist. Hitherto, as pointed out above, five isomeric oleic acids have been found to occur in nature, and in addition thereto, besides geometrical isomerides, some other synthetical oleic acids, such as $\alpha\beta$ and $\lambda\mu$ acids, have been obtained. *Fokin*[2] is of the opinion that oleic acids with a double linkage in an odd-even position ($\eta\theta$, $\iota\kappa$, $\lambda\mu$) are solid, whilst those with this linking in an even-odd position ($\theta\iota$, $\kappa\lambda$) are liquid. This rule can, however, only be looked upon as expressing a few facts, since the geometrical configuration also plays an important part; thus oleic and elaïdic acids, both of which have the double linking in the θ and ι position, represent the types of liquid and solid acids respectively.

(*a*) Ordinary Oleic Acid,[3] 9,10, or $\theta\iota$ Oleic Acid,



$$\begin{array}{l} CH_3\,.\,(CH_2)_7\,.\,CH \\ \qquad\qquad\quad \| \\ \qquad\qquad\quad CH(CH_2)_7\,.\,COOH. \end{array}$$

Ordinary oleic acid is found in most vegetable and animal fats, especially in the liquid ones, in combination with glycerol.

The chemically pure product can only be obtained with difficulty. A number of preparations sold commercially as " pure " oleic acid are obtained from almond oil by separating the ether-soluble lead salts from those of the solid acids, but it should be noted that oleic acid so prepared still contains small quantities of less saturated acids (linolic, and perhaps linolenic). On the other hand, oleic acid obtained on a large scale from tallow retains a small proportion of solid acids. The author lays stress on these points, as a number of observations on oleic acid (so-called *acid. oleic. puriss*) have been made with an impure acid, and hence statements as to the solubility of the salts prepared with such acid must be accepted with reserve. Oleic acid can only be considered as chemically pure if its iodine value is 90 (theoretical value 90·07). Most so-called pure oleic acids obtained in commerce deviate widely from this number, according as to whether they contain solid acids or less saturated acids; even the best preparations have iodine values varying from 82 to 84 on the one hand, and from 100 to 110 on the other. This has been confirmed by *Fahrion*,[1] who found in a chemically pure oleic acid, sold as free from linolic acid, 5 per cent of neutral substances and about 1 per cent of palmitic acid. After removal of these impurities the purified oleic acid still showed the iodine value 92·3.

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[1] Langer, *Arch. d. Pharm.*, 1889 (27), 241, 289, 625; Rathje, *ibid.*, 1908, 699.

[2] *Journ. Russ. Phys. Chem. Soc.*, 1912 (44), 653.

[3] The older formula, $CH_3\,.\,(CH_2)_{13}\,.\,C:CH\,.\,CH_2\,.\,COOH$, given by Saytzeff, *Berichte*, 1894 (27), Ref. 577, has been shown to be untenable by Baruch, *Berichte*, 1894 (27), 173 (cp. Le Sueur, *Journ. Chem. Soc.*, 1904, 1710; N. and Al. Saytzeff, *Journ. f. prakt. Chem.*, 1905 (71), 422).

On account of the change which oleic acid undergoes on heating with melted caustic potash (formation of palmitic acid), the constitutional formula of a 2,3 oleic acid (α, β oleic acid), $C_{15}H_{31}\,.\,CH=CH\,.\,COOH$, was previously ascribed to it. The true α, β oleic acid was prepared by G. Ponzio (*Atti R. Acc. Sc. Torino*, 1905, 970) and also by Le Sueur (*Journ. Chem. Soc.*, 1904, 1709).

In the opinion of A. A. Shukoff and P. J. Schestakoff (*Journ. Russ. Phys. Chem. Soc.*, 1908 (40), 830) the ordinary oleic acid separated from fats is not a chemical individual, but consists probably of a mixture of isomerides having a pair of doubly-linked carbon atoms in the 9,10 (θ,ι) position on the one hand, and in the 3,4 (β,γ) or 4,5 (γ,δ) position on the other. The 9,10 (θ,ι) acid was prepared from ι (or 1,10) hydroxystearic acid, and was found to yield about 10 per cent of γ-stearolactone when treated with zinc chloride (cp. "Stearolactone," p. 226).

Pure oleic acid is best prepared from tallow (which practically does not contain any less saturated acids than oleic acid), by saponifying with caustic potash, precipitating the soap solution with lead acetate, and extracting the dried lead salt with ether. The dissolved lead salt is decomposed with hydrochloric acid under ether, the liberated acid dissolved in ammonia and the solution precipitated with barium chloride. Next, the barium salt is dried, boiled out with hot alcohol, and the hot solution allowed to crystallise. The crystallised salt is decomposed either by a strong mineral acid or by tartaric acid (*Gottlieb*).[2] Exclusion of atmospheric air, although desirable, is not an essential condition, for the older statements, that oleic acid absorbs oxygen from the air with avidity, are erroneous. (These statements are due to the fact that the fatty acids from linseed oil or semi-drying oils were previously termed oleic acid.) Oleic acid prepared in this manner still contains solid acids. To remove the latter the conversion of the oleic acid into its chloro-iodo-product may be suggested. The latter can be separated from the saturated acids by dissolving in an organic solvent and allowing to crystallise. From the crystallised chloro-iodo-oleic acid, oleic acid would be obtained by heating with aniline or quinoline. *Farnsteiner* claims to have obtained pure oleic acid from olive oil by converting the mixed liquid olive oil acids into barium salts, and crystallising the latter repeatedly from benzene containing a little alcohol (cp. Chap. VIII.).

Pure oleic acid is a colourless liquid free from odour. It crystallises in the form of needles, solidifying at 4° C. and melting at 6·5° C. (*Partington* [3]).

Gottlieb [2] gave the melting point as 14° C. As at the time of the publication of his paper oleic acid could not be freed thoroughly from solid acids, the high melting point given by *Gottlieb* might have been explained, in the light of *Partington's* figure, as being due to dissolved palmitic and stearic acids. This explanation, however, becomes somewhat unsatisfactory, since *A. Kirschner*[1] stated that on allowing impure oleic acid to crystallise at 8°-10° C. he obtained a new crystalline form having a higher melting point than 14° C., viz. 16° C. It would therefore appear that oleic acid is dimorphous. On melting the crystals of melting point 16° C., and (more rapidly still) by cooling on ice, they are converted into crystals of lower melting point.

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[1] *Chem. Zeit.*, 1909, 429.

[2] *Journ. Chem. Soc.*, 1911, 316.

[3] *Liebig's Annal.*, 1846 (57), 38.

Chevreul gave the specific gravity at 14° C. as 0·898. More recent observations have led to the following numbers :—$d\frac{11 \cdot 8^\circ}{4^\circ}$ C. = 0·8908, $d^{15} = 0{\cdot}898$, $d^{20} = 0{\cdot}895$, $d^{30} = 0{\cdot}889$, $d^{50} = 0{\cdot}875$, and $d\frac{78 \cdot 4^\circ}{4^\circ} = 0{\cdot}854$. The following table contains the numbers obtained by *Procter*[2] for a specimen of " fairly pure " oleic acid :—

Temperature. ° C.	Specific Gravity.	Refractive Index.	Refractive Constants. $\frac{n-1}{d}$.	Refractive Constants. $\frac{n^2-1}{(n^2+2)d}$.
15	0·898	1·4638	0·5165	0·3072
20	0·895	1·4620	0·5159	0·3070
25	0·893	1·4603	0·5154	0·3069
30	0·889	1·4585	0·5158	0·3072
35	0·885	1·4566	0·5160	0·3075
40	0·882	1·4546	0·5154	0·3074
45	0·880	1·4528	0·5145	0·3071
50	0·875	1·4509	0·5153	0·3077
60	0·870	1·4471	0·5140	0·3072

On distilling oleic acid under ordinary pressure, it is partially broken up into water, and into carbonic, acetic, caprylic, and capric acids; at the same time sebacic acid[3] and hydrocarbons are formed. *Hviid*[4] states that oleic acid heated to about 350°-375° C. yielded 23·4 per cent of a distillate consisting of hydrocarbons, whereas the acid heated in the same manner in the presence of a hydrosilicate (cp. p. 46) yielded 79 per cent of a distillate consisting chiefly of hydrocarbons. In a current of superheated steam, however, it passes over unchanged at a temperature of about 250° C. This is indeed the method by which commercial oleic acid is prepared on the manufacturing scale in candleworks (see Vol. III. Chap. XV.). The following boiling points have been found by *Krafft and Nördlinger*,[5] and by *Krafft and Weilandt*:[6]—

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[1] *Zeits. f. physiol. Chem.*, 1912 (79), 759.

[2] *Journ. Soc. Chem. Ind.*, 1898, 1022.

[3] Redtenbacher suggested (*Liebig's Annal.*, 1840 (35), 208), as the most convenient method for the detection of oleic acid, to prove the presence of sebacic acid among the products of dry distillation. In the present state of our knowledge this method is no longer required.

[4] *Petroleum*, 1911 (6), 429.

[5] *Journ. Chem. Soc.*, Abstr., 1889, 691.

[6] *Berichte*, 1896, 1324.

Boiling Point. °C.	Pressure. mm. Mercury.
153·0[1]	0
223·0	10
232·5	15
249·5	30
264·0	50
285·5-286·0	100

C. Fischer and O. Harries[2] give 166° for a pressure of 0·25 mm. (temperature of bath 200° C.).

Oleic acid is insoluble in water, but dissolves readily in cold alcohol, even if the alcohol be somewhat dilute. On adding large quantities of water to the alcoholic solution, the acid is thrown out. On the greater solubility of oleic acid in mixtures of water, alcohol, and acetic acid, compared with that of the solid fatty acids palmitic and stearic, *David*[3] based a method of separating oleic acid from the solid acids.

Nitrous acid converts oleic acid at the ordinary temperature[4] into elaïdic acid. The same change takes place when the acid is treated with sodium bisulphite under pressure at 175°-180° C., or with sulphurous acid under pressure at 200° C. The change, however, is not complete, as the reaction is a reversible one.[5]

On exposure to light and air, oleic acid turns yellow or yellowish, acquires a rancid smell, and reddens blue litmus paper. *Scala*[6] isolated from oleic acid exposed to light and air the following products: œnanthaldehyde, formic, acetic, butyric, and œnanthic acids, and some dibasic acids assumed to be azelaïc and suberic acids (and dihydroxystearic acid?). (The same substances were obtained from a very rancid olive oil; cp. p. 54.)

A sample of oleic acid kept for about nineteen years (*Senkowski*[7]) deposited crystals melting at 48° C., whereas the unchanged oleic acid, as calculated from the iodine value of the sample, formed only 32·1 per cent of the whole mass. In the deposited crystals 8·3 per cent (calculated to stearolactone) of an ester were found. It is doubtful whether the remainder consisted of hydroxystearic acid. What change did occur in this oleic acid has not been further explained. From my own experience I can, however, state that a sample of commercial oleic acid from tallow, kept over sixteen years in an iron drum, which was very frequently opened, had retained its original neutralisation value, and practically its original iodine value, viz. 84.

After blowing air through oleic acid at 120° C. for 2, 4, 6, and 10 hours, the author found[8] respectively 0·62, 2·6, 3·5, and 6·0 per cent of "oxidised" acids (insoluble in petroleum ether) in the "blown" acid ; the specific gravities rose in the same order from 0·8980 to 0·9098, 0·9121, 0·9123, and 0·9238. Similarly, on digesting oleic acid with sulphur at a temperature between 130° and 150° C. sulphur is absorbed, without evolution of sulphuretted hydrogen ; apparently an addition product is formed (see Vol. III. Chap. XV. " Vulcanised Oils "). At higher temperatures, from 200° to 300° C., sulphuretted hydrogen is evolved.

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[1] Cp. Caldwell and Hurtley's results, table, p. 120.

[2] *Berichte*, 1902, 2162.

[3] *Journ. Chem. Soc.* 34, 1011.

[4] Lidoff states (*Analyst*, 1895, 178) that by the action of nitrous oxide on oleic acid at 80°-85°C. an increase of weight takes place, and the iodine value of the product falls to 9. Experiments made by Lewkowitsch show, however, that elaïdic acid is formed and the apparent low iodine value is due to the action of nitrous acid, left in the fatty acid, on potassium iodide (*Journ. Soc. Chem. Ind.*, 1897, 390).

[5] Cp. Albitzky, *Journ. f. prakt. Chem.*, 1903.

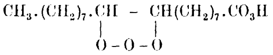
[6] *Staz. Sper. agr. ital.* 30, 613.

[7] *Zeits. f. physiol. Chem.*, 1898, 434; cp. also Salkowski, *Zur Kenntniss der Fettwachsbildung*, 1891, Berlin, p. 24.

[8] Lewkowitsch, *Analyst*, 1899, 322.

On oxidising oleic acid with nitric acid the following dibasic acids, adipic, pimelic, and suberic acids, were obtained ;[1] simultaneously volatile acids, from formic acid up to, and including, capric acid, were formed. Potassium permanganate, acting in acid solution on oleic acid, yields considerable quantities of dibasic acids. On oxidising oleic acid with an excess of potassium permanganate in dilute alkaline solution in the cold, dihydroxystearic acid is formed chiefly. *Edmed*[2] states that on oxidising oleic acid at 60° C., he obtained 60 per cent of dihydroxystearic acid, a small quantity of pelargonic acid, 16 per cent of azelaïc acid, and 16 per cent of oxalic acid.[3] If the oxidation with potassium permanganate be carried out in presence of only so much caustic potash as is required to neutralise the oleic acid employed, ketohydroxystearic acid is obtained in addition to dihydroxystearic acid.[4] On oxidising oleic acid with persulphuric acid (*Caro's* reagent) dihydroxystearidic acid is formed.[5]

Oleic Acid Ozonides.—According to *Molinari*[6] one molecule of ozone is assimilated with the formation of oleic acid ozonide, $C_{18}H_{34}O_5$, when ozone (ozonised air) is passed through oleic acid. *Harries*[7] has, however, shown that when an excess of ozone is used, the *first* product obtained by treating oleic acid with ozonised oxygen is not oleic acid ozonide, as the latter assimilates, on prolonged treatment with ozone, more oxygen, forming (by the absorption of a fourth atom of oxygen, in addition to one molecule of ozone) a perozonide. To this perozonide, ozonide peroxide, $C_{18}H_{34}O_6$, *Harries*[8] ascribes the following formula :



$$CH_3.(CH_2)_7.\underset{|}{CH} - \underset{|}{CH}(CH_2)_7.CO_3H \quad (O-O-O)$$

By washing with water and sodium carbonate this perozonide is converted into the normal ozonide, $C_{18}H_{34}O_5$, of the formula :

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[1] Lewkowitsch, *Journ. f. prakt. Chem.*, 1879, 159.

[2] *Journ. Chem. Soc.*, 73, 627.

[3] Link, in the author's laboratory, found that considerable proportions of oleic acid escape oxidation.

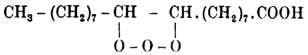
[4] Holde and Marcusson, *Berichte*, 1903, 2657 ; cp. N. and Al. Saytzeff, *Journ. f. prakt. Chem.*, 1905 (71), 421.

[5] Albitzky, *Berichte*, 1900, 2909 ; 1903 (67), 289, 357.

[6] Molinari, *Annuario della Soc. Chimica di Milano*, 1903, ix. 507 ; 1905, xi. 80 ; 1906, xii. fascie i. u. ii. ; iii. u. iv. *Berichte*, 1906, 2735 ; *Gazz. Chim.* 36, ii. 292 ; *Berichte*, 1907, 4154 ; 1908, 585 ; 2794.

[7] *Liebig's Annal.*, 343, 311 ; 374, 290 ; *Berichte*, 1906, 3729 ; 1907, 4906. Cp. also *ibid.*, 1906, 3732 ; Thieme, *Inaug. Dissert.*, Kiel, 1906 ; Harries, *Berichte*, 1912, 936 ; *Liebig's Annal.*, 1912 (390), 235.

[8] *Liebig's Annal.*, 1910 (374), 358.



$$CH_3-(CH_2)_7-\underset{|}{CH}-\underset{|}{CH}.(CH_2)_7.COOH \quad (O-O-O)$$

which *Molinari* had obtained straightway.

(*a*) *Oleic acid ozonide*, $C_{18}H_{34}O_5$, prepared according to the method described by *Molinari*,[1] forms a viscous, yellowish oil; $d^{18}=1{\cdot}0218$, $d^{22}=1{\cdot}0205$. *Harries and Franck* give $d^{20\cdot5}_{20\cdot5}=1{\cdot}0281$, $d^{20}_{4}=1{\cdot}0216$, and $n^{20}_{D}=1{\cdot}46021$. It is easily soluble in benzene and in chloroform, soluble in carbon bisulphide and in absolute alcohol, and sparingly soluble in cold petroleum ether. On warming the ozonide on the water-bath under a reflux condenser with a saturated solution of potassium bisulphite, the following *acids* are formed: azelaïc, nonylic (nonoic), an acid $C_{18}H_{32}O_6$, and a hydroxystearic acid (formed by the condensation of nonaldehyde and nonylic acid). In addition to the foregoing acids there are produced semi-aldehydes and nonylaldehyde; the latter undergoes polymerisation on being liberated from its bisulphite compound, to form paranonaldehyde $(C_9H_{18}O)_3$.[2]

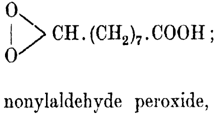
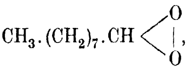
Harries,[3] maintaining his previously raised strictures on some of *Molinari's* statements, shows that on treating a solution of oleic acid in glacial acetic acid or carbon tetrachloride with either slightly (0·4 per cent of ozone) or strongly ozonised air (18 per cent of ozone), until a drop of the solution no longer decolourises bromine or iodine, the *normal ozonide* is always obtained. As soon, however, as the saturation point is exceeded the *perozonide* is formed.

The ozonide still retains its character as an acid since its ammonium, sodium, and copper salts can be isolated, although the salts are easily decomposed (*Harries and Franck*[4]).

(*b*) The *perozonide*, $C_{18}H_{34}O_6$, is more viscous than the normal ozonide, $d^{22\cdot5}_{22\cdot5}=1{\cdot}049$; $n^{22\cdot5}_{D}=1{\cdot}47113$. On shaking with sodium bicarbonate and water it is converted into the normal ozonide.

After prolonged treatment of the perozonide with ozonised air a superperoxide, superperozonide, $C_{18}H_{34}O_7$, is formed.

Both ozonides are converted by heating with water almost quantitatively into nonyl aldehyde and nonylic acid on the one hand, and into the semi-aldehyde of azelaïc acid and azelaïc acid on the other. No evolution of gas can be observed, and the presence of hydrogen peroxide can be detected. If, however, sodium hydrate be added to the water and the mixture then be boiled, sodium peroxide is formed which oxidises the aldehydes formed, being itself reduced to sodium hydrate. (The sodium hydrate so formed converts unchanged aldehydes into the decomposition products described by *Molinari*, who effected the decomposition of the ozonide by means of alkali.) The formation of nonylic and azelaïc acids would seem to prove the correctness of the constitutional formula ascribed above to oleic acid (cp. p. 178).

The decomposition of the ozonides also takes place in anhydrous solvents, such as glacial acetic acid or alcohol, on warming. With glacial acetic acid even more peroxide is formed than with water (*Harries*). In fact, on warming the glacial acetic acid solution vigorous evolution of gas is observed; since, however, the gas contains carbonmonoxide and carbondioxide it is evident that further complicated decomposition products are formed. It therefore follows that water does not play the important part in the decomposition of the ozonides which *Harries* previously ascribed to it. The decomposition of the oleic acid ozonide in glacial acetic acid is explained by *Harries* to take place in two directions. In one direction there is formed nonylaldehyde, $CH_3.(CH_2)_7.CHO$, and azelaïc semi-aldehyde peroxide  $\left.\begin{array}{l}O\\|\\O\end{array}\right>CH.(CH_2)_7.COOH$; and in the second direction there is formed nonylaldehyde peroxide,  $CH_3.(CH_2)_7.CH\left<\begin{array}{l}O\\|\\O\end{array}\right.$, and an azelaïc-semi-aldehyde $O{:}CH.(CH_2)_7.COOH$. The latter would then be converted into the semi-aldehyde of azelaïc acid by losing one atom of oxygen.

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[1] Molinari, *Berichte*, 1906, 2737.

[2] Molinari and Barosi, *ibid.*, 1908, 2794.

[3] Harries and Franck, *ibid.*, 1909, 446; 1910, 357.

[4] *Liebig's Annal.*, 1910 (374), 367.

The ozonides are saturated substances which do not decolourise bromine solutions. They are, however, capable of acting as oxidising substances, inasmuch as they liberate iodine from potassium iodide. (Hence in the "iodine test" the ozonides liberate iodine; probably one atom of iodine for each molecule of ozone (*Molinari* and *Fenaroli*).)

(*c*) *Oleic acid superperozonide* is formed from the perozonide. It can be obtained in a shorter time from oleic acid itself, by treating oleic acid, dissolved in 3 volumes of glacial acetic acid, for 4 hours with ozonised air containing 16 to 18 per cent of ozone, distilling off the glacial acetic acid *in vacuo*, and drying the residue over solid caustic potash and concentrated sulphuric acid. The product is a colourless viscous liquid, $d^{22°}_{22}=1{\cdot}079$; $n^{22°}_{D}=1{\cdot}46817$. On warming with water, it is broken down into the same decomposition product which the above described ozonides yield.[1]

For the interaction of oleic acid with nitrogen tetroxide see p. 175.

Oleic acid absorbs one molecule of *bromine* with the formation of oleic dibromide (dibromostearic acid);[2] similarly iodochloride is absorbed to form a saturated acid. On reducing these products with zinc and hydrochloric acid, oleic acid is regenerated (*Lewkowitsch*). On heating the dibromide with alcoholic potash, stearolic acid, melting point 48° C., is obtained (cp. "Petroselinic Acid").[3]

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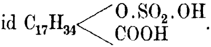
[1] C. Harries and W. Franck, *Liebig's Annal.*, 1910 (374), 361.

[2] The barium salt of the dibromostearic acid is wax-like, sparingly soluble in alcohol or ether at the ordinary temperature, but readily soluble in a mixture of alcohol and benzene (Farnsteiner, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1899, 15). The lead salt is viscous, sparingly soluble in cold 95 per cent alcohol, but dissolves readily in ether, petroleum ether, ether-alcohol, benzene, and a mixture of benzene and alcohol.

[3] Fokin (*Journ. Russ. Phys. Chem. Soc.*, 1912 (44), 155) states that monobromostearic acid from oleic acid and hydrobromic acid yields, on treatment with zinc dust and water in a sealed tube, stearic acid. In the case of the corresponding chloro-compound,

The action of *melting caustic potash* on oleic acid has been referred to above (p. 158 and p. 173).

Oleic acid dissolves in *concentrated sulphuric acid* in the cold without decomposition (*Chevreul*), and forms stearic acid hydrogensulphate, $C_{18}H_{35}(SO_4H)O_2$. On boiling this product with water, sulphuric acid is split off, and ι-hydroxystearic acid is formed, conjointly with a small quantity of stearolactone (*Geitel*)[1]; (see Vol. III. Chap. XV. "Turkey-red Oil").[2] A similar change takes place on heating oleic acid with zinc chloride to 185° C. (see Vol. III. Chap. XV. "Conversion of Oleic Acid into Candle Material"). In *Saytzeffs'*[3] opinion, the interaction of sulphuric acid with oleic acid leads to the formation of hydroxystearosulphuric acid  $C_{17}H_{34}\begin{cases}O.SO_2.OH\\COOH\end{cases}$. On boiling the latter with water a mixture of hydroxystearic acid and anhydrides of this acid is obtained; this mixture is sparingly soluble in 80 per cent alcohol. The anhydrides may be approximately differentiated into several individuals by the facility with which they are converted into salts of hydroxystearic acid on heating with alkalis. Fuller consideration to the action of sulphuric acid on oleic acid will be given in Vol. III. Chap. XV.

Sulphuric acid of 85 per cent strength is stated by *Twitchell* to have a similar action to that of concentrated acid.[4]

The *reduction of oleic acid to stearic acid* has been frequently attempted, and has formed one of the most fascinating problems in the fat industry.[5] *Goldschmidt*[6] was the first to attempt the reduction of oleic acid by heating it with fuming hydriodic acid and amorphous phosphorus for 8 to 10 hours in a sealed tube at 200°-210° C.; he thus obtained stearic acid. *P. de Wilde and Reychler*,[7] following *Goldschmidt*, tried to convert oleic acid into stearic acid by heating the former with 1 per cent of iodine in autoclaves at 270°-280° C. A mixture of fatty substances melting from 50° to 55° C. resulted; this was separated by distillation in a current of superheated steam into a residue insoluble in alcohol, a distillate containing stearic acid, and a liquid, which could not be converted into stearic acid by again subjecting it to the same treatment. The yield of stearic acid reached only 70 per cent, and no more than one-third of the iodine used could be recovered. The costliness of the process naturally prevented its commercial application.

The several attempts which were made subsequently to solve this important technical problem were discussed at length by *Lewkowitsch*[8] in 1897 and 1908; they will be more fully considered in Vol. III.

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the product consists of approximately two-thirds of stearic acid and one-third regenerated oleic acid.

[1] Cp. also Ssabanejew, *Journ. Russ. Phys. Chem. Soc.*, 1885, i. 35, 87; *Berichte*, 1886, Ref. 239.

[2] Cp. also *Journ. Soc. Chem. Ind.*, 1897, 390.

[3] *Journ. f. prakt. Chem.* 35, 369 (1898), 57, 26.

[4] *Journ. Soc. Chem. Ind.*, 1897, 1002.

[5] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1897, 390.

[6] *Sitzungsb. d. K. K. Akad. der Wissensch.*, 1876 (72), ii. 366.

[7] *Bull. Soc. Chim.*, 1889 [3], 295.

[8] *Journ. Soc. Chem. Ind.*, 1897, 390; 1908, 489.

Chap. XV. under the heading "Conversion of Oleic Acid into Candle Material." Here it may suffice to state that *A. de Hemptinne*[1] succeeded in reducing oleic acid to stearic acid by silent electrical discharges in an atmosphere of hydrogen, but as not more than 50 per cent of oleic acid was converted into stearic acid by this method, it is useless as a commercial process. Complete reduction can be obtained by applying *Sabatier and Senderens'* catalytic process (nickel catalyst in a current of hydrogen). By this method *Bedford*[2] and *Lewkowitsch*[3] succeeded in reducing oleic acid to stearic acid with a practically theoretical yield. *Paal and Roth*[4] showed that oleic acid can be reduced in the cold by means of hydrogen in the presence of colloidal palladium. They thus obtained from oleic acid 60 per cent of the theoretical yield of stearic acid. (With regard to the formation of isoöleic acid, see above, p. 173).

On heating oleic acid with zinc powder to a temperature of about 350° C., there are formed carbon dioxide, hydrogen, hydrocarbons, liquid and solid olefinic hydrocarbons, the bulk of which distils at 270° to 300° C., and contains eighteen atoms of carbon in the molecule.[5] There are further formed a certain amount of lower hydrocarbons, as also higher hydrocarbons, thus indicating that degradation as well as polymerisation run concurrently with the principal reaction.

By heating oleic acid with zinc dust in a current of hydrogen at a temperature of about 250° C. the author found (in conjunction with *Pick*[6]) that a large amount of oleic acid was converted into hydrocarbons; at a temperature of about 350° C. complete conversion into gas and hydrocarbons took place. If the temperature was kept below 200° C., very little destruction of oleic acid occurs.

Lifschütz[7] indicated a spectroscopic method for the recognition of the smallest quantities of oleic acid in the presence of other acids.

With regard to the separation of oleic acid from saturated acids, as also from less saturated fatty acids, compare Chapter VIII.

For oleic anhydride see above, p. 147.

Potassium oleate, $KC_{18}H_{33}O_2$, forms a transparent, jelly-like mass, which is far more readily soluble in water, alcohol, and ether than the sodium salt. One part of the salt requires for complete solution 4 parts of water, or 2·15 parts of alcohol, or 29·1 parts of boiling ether.

Sodium oleate, $NaC_{18}H_{33}O_2$. The pure salt is prepared by crystallisation from absolute alcohol (not from dilute alcohol). It dissolves in 10 parts of water at 12° C., or in 20·6 parts of alcohol, specific gravity 0·821, at 13° C. It also dissolves in 100 parts of boiling ether. The anhydrous salt melts at 232°-235° C.

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[1] English patent. 1572, 1905; French patent 349,942; German patent 167,107; United States patent 797,112.

[2] *Inaug. Dissert.*, Halle a/S., 1906,

[3] *Journ. Soc. Chem. Ind.*, 1908, 489.

[4] *Berichte*, 1908, 2283.

[5] Hébert, *Bull. Soc. Chim.*, 1903, 316.

[6] Unpublished experiments; cp. also *Berichte*, 1907, 4161.

[7] Hoppe-Seyler's *Zeits. f. physiol. Chem.*, 1908 (56), 446. Cp. also A. Manea, *Chem. Zentralbl.*, 1908, ii. 1702.

Lithium oleate, $LiC_{18}H_{33}O_2$, is soluble in hot alcohol, insoluble in ether, carbon bisulphide, and benzene. 100 c.c. of water dissolve at 18° C. 0·0674 gram, and at 25° C. 0·132 gram. 100 c.c. of alcohol of the specific gravity 0·797 dissolve at 18° C. 0·9084 gram, and at 25° C. 1·009 gram.[1]

Ammonium oleate, $NH_4.C_{18}H_{33}O_2$. The solubilities of the ammonium salt in alcohol, ether, and acetone have been given above, p. 140). According to *Wallerant*[2] ammonium oleate forms "liquid crystals," but *A. Moldziejowski*[3] showed that the "liquid crystals" can be obtained by evaporating the aqueous or alcoholic solution at the ordinary temperature; hence the observed structures must be looked upon rather as an emulsion than as liquid "crystals."

The metallic oleates behave with water much in the same manner as do the metallic salts of palmitic and stearic acids; they are mostly soluble in alcohol, benzene, chloroform, carbon tetrachloride, carbon bisulphide, nitrobenzene, pyridine, and petroleum ether;[4] some are also soluble in ether (cp. Vol. III. Chap. XV. "Salts of the Alkaline Earths and Heavy Metals").

Calcium oleate, $Ca(C_{18}H_{33}O_2)_2$, forms a powder which is insoluble in alcohol and ether. It is somewhat soluble in concentrated sugar solution: thus 200 c.c. of a 10 per cent sugar solution, after digestion with oleate for one hour, dissolve at 19·5° C., 35° C., 50° C., and 65° C., 0·0661, 0·1767, 0·450, and 0·726 grm. respectively.[5] Calcium oleate in a solution of pyridine passes through an india-rubber membrane.

Barium oleate, $Ba(C_{18}H_{33}O_2)_2$, is a crystalline powder insoluble in water, and but sparingly soluble in boiling alcohol. At 100° C. it conglutinates without, however, becoming liquid. Dried barium oleate[6] is very sparingly soluble in hot benzene; in a mixture of hot benzene and absolute alcohol it dissolves with great difficulty on boiling. In the presence of small amounts of water, however, barium oleate easily dissolves in hot benzene; thus it is sufficient to admix with benzene 5 per cent, or even less, of 95 per cent alcohol to effect solution. The salt separates out from the hot benzene solution on cooling almost completely (in the form of a crystalline powder consisting of long, very thin needles or laminæ of silvery lustre); 100 c.c. of the filtrate retain at 11° C. 0·015 grm., and at 17·5° C. 0·023 grm. of barium oleate. With chloroform and petroleum ether the salt shows a similar behaviour.

Aluminium oleate, $Al(C_{18}H_{33}O_2)_3$, forms a jelly-like mass, insoluble in alcohol, and sparingly soluble in hot ether, in petroleum ether, and benzene. In the arts it is used as an "oil-thickener" (cp. Vol. III. Chap. XV.).

Silver oleate, $AgC_{18}H_{33}O_2$, is almost insoluble in ether. (Difference from the silver salt of rosin acids.)

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[1] Partheil and Ferié, *Arch. d. Pharm.*, 1903, 545.

[2] *Compt. rend.*, 1906 (143), 693. [3] *Zeits. f. Krystall. und Miner.*, 1913 (52), 1.

[4] Cp. Kahlenberg, *Trans. Amer. Electrochem. Soc.*, 1905 (5), 167; Kahlenberg and Anthony, *Journ. de chimie physique*, 1906 (iv.), 358.

[5] *Zeits. f. angew. Chem.*, 1901, 1115.

[6] Farnsteiner, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901, 63.

Copper oleate, $Cu(C_{18}H_{33}O_2)_2$, melts at 100° C. to a green oil. It dissolves readily in cold ether (to a green solution), and also in alcohol (to a bluish-green solution). The salt crystallises in the shape of rods behaving like "liquid crystals."[1] Metallic copper dissolves in oleic acid with evolution of hydrogen.[2]

Lead oleate, $Pb(C_{18}H_{33}O_2)_2$ (known already to *Dioscorides*), is a white powder, melting at 45°-50° C. to a yellow oil.[3] It is soluble in ether,[4] and may thus be separated from the saturated acids (palmitic, stearic), and also from elaïdic acid. This separation, however, is not a complete one.[5] Lead oleate is also soluble in petroleum ether, but only slightly soluble in absolute alcohol (*Twitchell*).

Methylester, $d^{18} = 0{\cdot}879$; it boils at 212°-213° C. under a pressure of 15 mm.

Ethylester, specific gravity 0·871 at 16° C.[6]

Amylester, $d\frac{18}{4} = 0{\cdot}8886$, $d^{15} = 0{\cdot}897$; it does not solidify at 0° C.

In near relation to oleic acid stands its geometrical isomeride, *elaïdic acid*.

Elaïdic acid (discovered by *Boudet* in 1832 when studying the action of *Poutet's* reagent[7]) is obtained by allowing nitrous acid fumes, or a nitrite and nitric acid, to act on ordinary oleic acid at the ordinary temperature; after a short time the oleic acid is changed into its stereometrical isomeride, elaïdic acid.[8] The separation of elaïdic acid from unchanged oleic acid is readily effected by crystallisation from alcohol or ether, or by separating the lead salts by means of ether or benzene. Elaïdic acid is also obtained by the action of sulphurous acid or bisulphites under pressure at elevated temperatures on oleic acid.[9]

The acid crystallises from alcohol in plates melting at 44·5° C.[10] The same melting point was observed by the author in the case of a specimen of repeatedly crystallised elaïdic acid, prepared in his laboratory, as also of a specimen carefully purified by *Geitel*.[11] *Farnsteiner*[12] records the melting point 43·5°-44·5° C. Hence, *Saytzeffs'*[13] statement, that elaïdic acid melts at 51°-52° C. (and solidifies at 44°-45° C.), must be accepted with reserve. $d^{79.4°}_{4°}$ C. = 0·8505.

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[1] E. Richter, *Zeits. f. angew. Chem.*, 1907, 1613.

[2] C. B. Gates, *Journ. Phys. Chem.*, 1911 (15), 138.

[3] G. B. Neave, *Analyst*, 1912, 399. The older statement, Gottlieb's (*Liebig's Annal.*, 1845 [57], 38), that lead oleate melts at 80° C., must be abandoned.

[4] Gusserow, *Arch. d. Pharm.*, 1828 (27), 153. The lead salt of α-oleic acid is practically insoluble in ether.

[5] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1890, 845; cp. also Chap. VIII.

[6] For some suggested technical applications of the ethylester, cp. Dreymann, French patent 343,158; English patent 10,466, 1905.

[7] Cp. Laurent, *Annal. de Chim. et de Phys.* 65, 149.

[8] For the opinion of Gawalowski that two isomeric elaïdic acids are formed, cp. *Pharm. Post.*, 1905 (38), 97.

[9] Heating of 3·5 grms. of oleic acid with three drops of glacial acetic acid for thirty hours at 98° C. did not produce conversion into elaïdic acid; nor could conversion be affected by adding to the same quantity three drops of glacial acetic acid and three drops of water and heating as above. In neither case the product solidified on being inoculated with elaïdic acid. P. Rabe, *Berichte*, 1912, 2932.

[10] Cp. H. Meyer, *Liebig's Annal.*, 1840 (35), 182.

[11] *Analyst*, 1899, 258. [12] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1899, 5.

[13] *Journ. f. prakt. Chem.*, 1894 (50), 175.

Elaïdic acid distils almost unchanged at reduced pressure. The following boiling points were ascertained by *Krafft and Nördlinger* :—

Boiling Point. ° C.	Pressure. mm. Mercury.
154	0
225	10
234	15
251·5	30
266	50
287·8-288·0	100

Like oleic acid, elaïdic acid can be reduced to stearic acid by fuming hydriodic acid and phosphorus under pressure. Doubtless, catalytic reduction by means of hydrogen would effect the conversion more expeditiously.

Elaïdic acid can be converted in its turn into ordinary oleic acid by boiling iodostearic acid, prepared from elaïdic acid, with alcoholic potash ; simultaneously some " isoöleic " acid is formed.[1]

On heating elaïdic acid with sulphurous acid under pressure, about 20 per cent is converted into ordinary oleic acid.[2] By oxidation with potassium permanganate in alkaline solution in the cold, dihydroxystearidic acid is obtained,[3] whilst pelargonic, azelaïc, and oxalic acids are formed as secondary products. *Edmed*[4] ascertained the following percentages of oxidation products : dihydroxystearidic acid melting at 99° C., 33 per cent ; pelargonic acid, 13 to 14 per cent ; azelaïc acid, 26 per cent ; oxalic acid, 15-20 per cent (cp. above p. 182). *Caro's* reagent yields a dihydroxystearic acid which appears to be identical with the dihydroxystearic acid formed by oxidising elaïdic acid with potassium permanganate (*Albitzky*[5]). With melted caustic potash elaïdic acid, like ordinary oleic acid, yields palmitic acid. By the action of concentrated sulphuric acid on elaïdic acid, anhydrides are chiefly produced yielding ι-hydroxystearic acid on treatment with alcoholic potash.[6]

The behaviour of elaïdic acid to ozone simulates that of oleic acid, *i.e.* it forms an ozonide and a perozonide.[7]

From these reactions it would seem to follow that elaïdic acid is a stereometrical isomeride of oleic acid ; this may be expressed by the following synoptical formula :—

$$\begin{array}{r} CH_3(CH_2)_7 . CH \\ \| \\ COOH . (CH_2)_7CH. \end{array}$$

The *barium, lead,* and *silver* salts of elaïdic acid are sparingly soluble in alcohol and ether. *Lead* elaïdate simulates, as regards solubility, the lead salts of the solid saturated fatty acids (cp. p. 141). The following table gives some analytical data :—

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[1] Lebedeff, *ibid.*, 1894 (50), 61.

[2] Albitzky, *ibid.*, 1900 (61), 65.

[3] *Berichte*, 1894, 173.

[4] *Journ. Chem. Soc.*, 1898, 631.

[5] *Journ. f. prakt. Chem.*, 1903 (67), 357.

[6] Tscherbakoff and Saytzeff, *ibid.*, 1898 (57), 27.

[7] Harries and Thieme, *Liebig's Annal.*, 1905 (343), 354 ; Harries and W. Franck, *ibid.*, 1910 (374), 360.

100 c.c. of	Dissolve Lead Salt. Grms.	At ° C.
Ether	0·0016 to 0·0086	16-20
Benzene	0·0040	16-20
,, after dissolving the salt in the hot and allowing to crystallise.		
,, after 1 hour	0·0148	16
,, after 17 hours	0·0028	16
Absolute alcohol — after dissolving the salt in the hot and allowing to crystallise —after 18 hours	0·0100	17

Methylester, *d*18° C. = 0·872.

Ethylester, *d*18° C. = 0·868.

Other elaïdic acids obtained hitherto are :—

(1) *Tarelaïdic acid*, 6,7 elaïdic acid, from tariric acid [1] by converting it into its monohydriodic-addition derivative and reducing the latter with zinc dust and acetic acid. This tarelaïdic acid forms small compact prisms melting at 52·5° C. The acid does not assimilate iodine in acetic acid solution, but absorbs two atoms of bromine, and yields on oxidation with potassium permanganate *cis* 6,7, dihydroxystearic acid melting at 117·5° C.

(2) 8,9 *Elaïdic acid* (see under Isoöleic acid).

(3) 9,10 *Elaïdic acid* (see under Isoöleic acid).

(4) *Petroselin-elaïdic acid* (see under Petroselinic acid).

" Isoöleic " (" Para-oleic "), Solid Oleic Acid, is prepared, according to *M., C., and A. Saytzeff*,[2] by distilling ι-hydroxystearic acid under diminished pressure, when a mixture of ordinary oleic and isoöleic acids, together with some unchanged hydroxystearic acid, passes over. Isoöleic acid is isolated by allowing the mixture to crystallise from its ethereal solution and converting the crystallised acids into their zinc salts, which are exhausted with boiling alcohol, when zinc hydroxystearate remains undissolved ; on cooling the filtered alcoholic solution of zinc isoöleate and zinc oleate the former separates out. Isoöleic acid is then liberated from its zinc salt by dilute sulphuric acid and purified by repeated crystallisation from ether. The mixture of the two isomeric acids can be more readily resolved into its components by crystallisation from petroleum ether.[3]

Isoöleic acid is also formed when iodostearic acid, obtained from hydriodic acid and ordinary oleic or elaïdic acid, is heated with alcoholic potash under a reflux condenser. The product contains isoöleic acid, together with unchanged oleic acid. Isoöleic acid assimilates the elements of hydrogen iodide, giving a liquid iodostearic acid which yields, on treatment with alcoholic potash, one unsaturated acid only, viz. isoöleic acid (see above). From this *M. and A. Saytzeff* concluded that the iodine was attached to the α-carbon atom, and that the iodo-compound had the formula $C_{16}H_{33}.CHI.COOH$; hence they assigned to isoöleic acid the formula $CH_3(CH_2)_{14}CH=CH.COOH$. This constitution has, however, been shown, by *Le Sueur*,[1] to be erroneous. For on treating the above iodostearic acid with silver oxide a mono-hydroxyderivative melting at 82-85° C. was obtained. Since true α-hydroxystearic acid (*Le Sueur*) melts at 91-92° C., the hydroxystearic acid and the iodostearic acid which the *Saytzeffs* prepared cannot be α-derivatives. It should, moreover, be noted that the true α-iodostearic acid[2] is a crystalline substance melting at 66° C. By treating ordinary oleic acid with hydriodic acid and subsequently eliminating the latter, at least the following three reactions would seem to take place: (1) Conversion of oleic acid into its stereo-chemical isomeride; (2) migration of the double linking in the direction of the carboxyl group; (3) replacement of the iodine atom by hydroxyl.

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[1] Arnaud and Posternak, *Compt. rend.*, 1910 (150), 1130.

[2] M., C., and A. Saytzeff, *Journ. f. prakt. Chem.*, 1887 (35), 386 ; 1888 (37), 269.

[3] Shukoff and Schestakoff, *ibid.*, 1903 (67), 416.

Arnaud and Posternak[3] found, however, on repeating *Saytzeffs'* experiment that "isoöleic acid" is not a chemical individual, but represents a mixture of several "oleic" acids, from which the following substances have been isolated hitherto: (1) Ordinary 9,10 oleic acid, (2) ordinary 9,10 elaïdic acid, (3) an 8,9 elaïdic acid, (4) a hydroxystearic acid. These four products do not yet exhaust the number of acids occurring in the mixture hitherto considered to be isoöleic acid. Reasoning by analogy, the assumption is made by *Arnaud and Posternak* that a further isomeride of oleic acid (or of elaïdic acid) in which the double linking has been displaced in the opposite direction occurs in *Saytzeffs'* isoöleic acid; it is likely that a second hydroxystearic acid will be found in this mixture. From the data given by *Arnaud and Posternak* the composition of the mixture may be calculated to be approximately: 9,10 elaïdic acid, 15 per cent; hydroxystearic acid, 18 per cent; 8,9 and 9,10 elaïdic acids, 36 per cent; the remainder, containing ordinary oleic acid, is liquid.

Ponzio assigned to isoöleic acid the same constitutional formula as that given above (p. 178) for oleic acid.

Jegorow[4] ascribes to isoöleic acid melting point 42° C., prepared by *Saytzeff's* method, the constitutional formula $CH_3.(CH_2)_6.CH=CH.(CH_2)_8COOH$ (see above, p. 175).

In view of the discrepant observations detailed above, the nature of "isoöleic" acid is open to doubt. Since, however, considerable quantities of "isoöleic" acid occur in commercial stearic acid, obtained by "acid saponification" and subsequent distillation (cp. Vol. III. Chap. XV.), and a well crystallised product can be isolated, its characteristics are given in the following lines, with the reservation that these characteristics may belong to a eutectic mixture of several isomeric acids.

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[1] *Journ. Chem. Soc.*, 1904, 1709.

[2] Ponzio, *Gazz. chim. ital.*, 1904 (34), ii. 77.

[3] *Compt. rend.*, 1910 (150), 1520.

[4] *Journ. f. prakt. Chem.*, 1912 (86), 539.

Isoöleic acid is also formed in the catalytic reduction of oleic acid under certain conditions, especially if copper powder be used as the catalyst; it would appear as if the formation of isoöleic acid forms the first step in the hydrogenation process of oleic acid, the double linkage being forced to migrate from the central position towards the end of the chain. It would follow that isoöleic acid is more readily hydrogenated than oleic acid (*Lewkowitsch*).

"Isoöleic" acid forms transparent, rhombic plates (from ether), melting from 44° to 45° C. It is very easily soluble in alcohol, considerably less soluble in ether. Like ordinary oleic acid, it absorbs two atoms of bromine or iodine in the cold, and undergoes the same changes as does oleic acid when treated with melted caustic potash. Dibromo-isoöleic acid yields on treatment with silver oxide *p*-dihydroxystearic acid (cp. p. 229). Potassium permanganate yields a dihydroxystearic acid differing from that obtained from ordinary oleic acid (cp. p. 228). On treating isoöleic acid with concentrated sulphuric acid, and subsequently boiling the product with water, two isomeric hydroxystearic acids (see p. 225) are formed, differing in their behaviour when subjected to distillation *in vacuo*.

Calcium salt, $Ca(C_{18}H_{33}O_2)_2 + H_2O$, is insoluble in hot alcohol.

Lead salt is considerably less soluble in ether than is lead oleate.

(*b*) RAPIC ACID, $C_{18}H_{34}O_2$

Rapic acid occurs, according to *Reimer and Will*,[1] in the mixed rape oil fatty acids. The acid does not solidify on cooling, nor does it yield a solid isomeride with nitrous acid.

Reimer and Will assigned to this acid the formula of a hydroxylated acid, $C_{18}H_{34}O_3$, which is extremely unlikely, as the acetyl value of rape oil is very low (cp. Vol. II. Chap. XIV.). *Zellner*[2] showed later that rapic acid has the composition $C_{18}H_{34}O_2$, by converting it into an iodo-compound yielding stearic acid on reduction with zinc and hydrochloric acid.

The *sodium* salt forms a gelatinous mass easily soluble in water; the *zinc* salt is crystalline, dissolves easily in alcohol and ether, and melts at 78° C.

(*c*) PETROSELINIC ACID, $CH_3(CH_2)_{10}.CH{=}CH.(CH_2)_4.COOH$

The fatty oil of parsley seeds contains an "oleic" acid melting at 33°-34° C., solidifying at 27° C.; $n_D^{40} = 1{\cdot}4533$. This acid is optically inactive. Its iodine value was found to agree with that demanded by theory. Petroselinic acid behaves in many respects like ordinary oleic acid. Nitrous acid converts it into a stereoisomeride (an "elaïdic" acid), melting at 54° C. With potassium permanganate in alkaline solution petroselinic acid yields a dihydroxystearic acid, melting at 122° C. (see p. 229). By treatment with melted caustic potash, acetic and palmitic acids are obtained as the chief products of the reaction.

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[1] *Journ. Soc. Chem. Ind.*, 1887, 732.

[2] *Ibid.*, 1896, 661.

Petroselinic acid absorbs two atoms of bromine with formation of a dibromide, which furnishes on heating with (methyl- or ethyl-) alcoholic potash under pressure a " stearolic " acid, $C_{18}H_{34}O_3$, melting at 54° C., which would aptly be termed "petroselinolic acid." The ketonic acid obtained therefrom (melting at 80° C.) yields two stereoisomeric oximes, which are converted, by concentrated sulphuric acid, into amino acids. By heating the latter with concentrated hydrochloric acid, undecylamine, pimelic acid, and lauric acid were obtained; hence *Vongerichten and Köhler*[1] assigned to petroselinic acid the constitution expressed by the above given structural formula.

The *amide* crystallises in needles melting at 76° C.

The *barium* salt crystallises in anhydrous needles. The *lead* salt is sparingly soluble in cold ether, readily soluble in hot ether; it melts at 86° C.

(d) Cheiranthic Acid, $C_{18}H_{34}O_2$

This acid has been found amongst the mixed fatty acids of Cheiranthus oil (*Matthes and Boltze*[2]).

The acid forms white silky needle-shaped crystals melting at 30° C. $n_D^{40} = 1{\cdot}4535$. The iodine value of the acid is given as 71·16, whereas the theoretical value of an unsaturated fatty acid $C_{18}H_{34}O_2$ would be 90. The acid had been isolated by recrystallisation from alcohol of a fraction of the distilled fatty acid boiling between 240° and 245° at 12 mm. pressure. The neutralisation value of this fraction was 177·1 and the iodine value 78·1. These latter figures, as also the above given melting point, would speak much more for an " erucic " acid than for an " oleic acid "; this view is, however, not supported by the elementary analyses given for cheiranthic acid and the dihydroxystearic acid obtained therefrom.

By treatment with nitrous acid cheiranthic acid yields an isomeride which melts, after recrystallisation from absolute alcohol, at 51°-52° C. and has $n_D^{70} = 1{\cdot}4520$. By oxidation with potassium permanganate a dihydroxystearic acid is obtained melting at 180° and having $n_D^{60} = 1{\cdot}4570$. This dihydroxystearic acid differs from the known dihydroxystearic acids (described below).

It will be seen that cheiranthic acid very closely simulates petroselinic acid.

Other " oleic " acids which are probably identical with either cheiranthic or petroselinic acid have been found by *Scherer*[3] in the oils obtained from the seeds of *Pimpinella anisum* and *Fœniculum capillaceum*. These oils yielded respectively " oleic " acids of the melting points 30° C. and 30·5° C., and iodine values 73·5 and 86·15.

(e) Liver Lecithin Oleic Acid, $(CH_2)_{11}.CH{=}CH.(CH_2)_4COOH(?)$

An oleic acid isolated from liver lecithin differs, according to *Hartley*,[4] from ordinary oleic acid in that it yields, on oxidation, a dihydroxystearic acid melting at 129·5° C. Further oxidation of this dihydroxystearic acid with a hot solution of potassium permanganate yielded no trace of pelargonic nor of azelaïc acid. *Hartley*, however, found and identified amongst the products caproic acid, and also obtained (without, however, isolating the acid) some evidence as to the presence of a decamethylene dicarboxylic acid. *Hartley* ascribes to this oleic acid the constitution of a 6,7 oleic acid. This would, however, be contradicted by the constitution of petroselinic acid as given above. Moreover, *Hartley* states that this acid does not yield a solid isomeride on treatment with nitrous acid, whereas the 6,7 acid described above as petroselinic acid does yield a higher melting isomeride.

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[1] *Berichte*, 1909, 1638; cp. A. Köhler, *Inaug. Dissert.*, Weimar, 1909.

[2] *Arch. d. Pharm.*, 1912 (250), 211.

[3] *Inaug. Dissert.*, 1909, Strassburg.

[4] *Journ. f. Physiol.*, 1909 (38), 367.

DOEGLIC ACID, $C_{19}H_{36}O_2$

The existence of this acid, which is stated by *Scharling*[1] to occur in Arctic sperm oil as a dodecatyl ester, is doubtful. In *Bull's* opinion (see below) "doeglic" acid is a mixture of oleic and gadoleic acids.

JECOLEIC ACID, $C_{19}H_{36}O_2$

An acid of this composition is assumed by *Heyerdahl* to occur in cod liver oil,[2] he having obtained a dihydroxyjecoleic acid (cp. p. 230) on oxidising cod liver oil fatty acids with potassium permanganate. Jecoleic acid is stated to form at least 20 per cent of the liquid fatty acids in cod liver oil (cp. "Gadoleic Acid").

GADOLEIC ACID, $C_{20}H_{38}O_2$

This acid occurs, according to *Bull*,[3] in notable quantities in cod liver oil, as also in herring and whale oils. It was prepared by converting Lofotes cod liver oil glycerides into methylesters by treatment with sodium methylate, and fractionation of the methylesters *in vacuo.* The fraction boiling between 223° and 225° C. under 10 mm. pressure, and forming about 15 per cent of the total methylesters, yielded on saponification an acid melting at 24·5° C. The melting point remained unchanged even after repeated crystallisation from cold alcohol. The neutralisation value 180·5 and the iodine value 80·3 of the acid would seem to confirm the correctness of the formula $C_{20}H_{38}O_2$.

By oxidation with potassium permanganate in alkaline solution at 0° C., dihydroxygadoleic acid is obtained. *Bull* is of the opinion that *Scharling's* doeglic acid is a mixture of oleic and gadoleic acids.

The neutral, as also the acid, *potassium* salts are very sparingly soluble in cold alcohol.

The *lead* salt stands midway between oleic and erucic acids as regards its solubility in ether.

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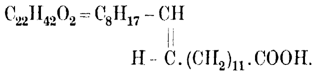
[1] *Journ. f. prakt. Chem.*, 1848 (43), 257.

[2] *Cod Liver Oil and Chemistry*, p. xcviii.

[3] *Berichte*, 1906, 3574.

Erucic Acid[1]



$$C_{22}H_{42}O_2 = \begin{array}{l} C_8H_{17}-CH \\ \qquad\quad \| \\ H-C.(CH_2)_{11}.COOH. \end{array}$$

Erucic acid (discovered by *Darby*[2] in 1849), occurs in rape oil (*Websky*),[3] in black and white mustard oils,[4] in fish oils,[5] whale oil, and in cod liver oil;[6] the solid glyceride in the oil from *Tropæolum majus* (Vol. II. Chap. XIV.) is almost pure tri-erucin. The dried root matter of *Beta vulgaris* contains approximately 18·6 per cent of erucic acid.[7] The formation of erucic acid from ligustrol has been referred to above (p. 1). The acid crystallises from alcohol in long, fine needles melting at 33°-34° C. The following boiling points were ascertained by *Krafft and Nördlinger*:—

Boiling Point. °C.	Pressure. mm. Mercury.
179	0
254·5	10
264	15
281	30

Erucic acid much simulates oleic acid in its properties. Thus it absorbs two atoms of bromine or iodine. (The dibromide forms crystals melting at 46°-47° C.) It also assimilates one molecule of ozone.[8] Like oleic acid it forms a perozonide (*Thieme*[9]). With nitrogen peroxide it gives an addition product which yields on decomposition with hydrochloric acid, nonylic and brassylic acids (see p. 175). Nitrous acid, as also sulphurous acid and bisulphites under pressure at high temperatures (cp. "Oleic Acid," p. 181), convert it into its stereometrical isomeride, *brassidic acid*, $C_{22}H_{42}O_2$.

By heating with fuming hydriodic acid and phosphorus[10] it is reduced to behenic acid. Complete conversion to behenic acid is readily obtained by reducing with hydrogen in the presence of nickel (*Lewkowitsch*[11]). Melting with caustic potash splits it into acetic and arachidic acids. Oxidation with potassium permanganate yields dihydroxybehenic acid. By oxidation with nitric acid, nonylic and brassylic acids are obtained.

The dibromide of erucic acid yields on treatment with alcoholic potash, a behenolic acid, a homologue of stearolic acid (see p. 236). From the behenolic acid a keto-acid and its oximes are obtained similarly as has been described above for oleic acid. These oximes are then broken down into pelargonic acid and 13 aminobrassylic acid on the one hand, and into octylamine and brassylic acid on the other. By these reactions the constitutional formula above given is confirmed.

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[1] Liebermann, *ibid.*, 1893, 1869; cp. also Alexandroff and N. C. Saytzeff, *Journ. f. prakt. Chem.*, 1894 (49), 63.

[2] *Liebig's Annal.*, 1849 (69), 1.

[3] *Jahresbericht Fortsch. d. Chem.*, 1853, 443; cp. also Reimer and Will, *Berichte*, 1886, 3320; cp. also "Yellow Acacia Oil," Vol. II. Chap. XIV.

[4] The occurrence of erucic acid in grape seed oil (Fitz, *Berichte*, 1871, 444) is doubtful; cp. Vol. II. Chap. XIV. "Grape Seed Oil."

[5] Bull, *Chem. Zeit.*, 1899, 996.

[6] Bull, *Berichte*, 1906, 3570.

[7] E. Neville, *Journ. Chem. Soc.*, 1912, 1104.

[8] Cp. T. Weyl, English patent 11,165, 1901.

[9] *Inaug. Dissert.*, Kiel, 1906.

[10] G. Goldschmidt, *Sitzungb. d. K. K. Akad. d. Wissensch.*, 1876 (72), ii. 366.

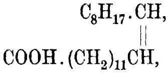
[11] Unpublished observation; cp. also Chap. VIII. "Erucic acid."

The *ammonium* salt melts from 70°-77° C.; it is soluble in methyl- and ethyl-alcohol, sparingly soluble in ether, benzene, chloroform, cold carbon bisulphide, and carbon-tetrachloride (*Falciola* [1]).

The *sodium* salt of erucic acid melts at 230°-235° C. The *lead* salt is but sparingly soluble in ether, differing in this respect from lead oleate.

Ethylester, boils above 360° C. without decomposition.

Brassidic acid,



$$\begin{array}{r} C_8H_{17}.CH, \\ \| \\ COOH.(CH_2)_{11}CH, \end{array}$$

crystallises from alcohol in laminæ melting at 65° C., and solidifying at 56° C.; it boils *in vacuo* at 180° C., and under a pressure of 15 mm. at 265° C. The acid stands in the same relation to erucic acid as elaïdic acid does to oleic acid. By treatment with phosphorus and fuming hydriodic acid it is converted into behenic acid.[2]

Sodium salt, melts at 245°-248° C. The *lead salt* is sparingly soluble in hot ether.

Ethylester, crystallises from alcohol in shining laminæ, melting at 29°-30° C., and boiling above 360° without undergoing decomposition.

"Isoerucic" acid, is obtained by boiling iodo-behenic acid with alcoholic potash. The iodo-behenic acid may be prepared from either erucic or behenic acid [3] (cp. "Isoöleic Acid," p. 190). *Ponzio*,[4] rejecting *Saytzeff's* formula $CH_3.(CH_2)_{17}.CH_2.CH{=}CH.COOH$,[5] is of the opinion that the constitution of isoerucic acid is expressed by the same formula as that of erucic acid.

Isoerucic acid crystallises from alcohol in plates melting at 54°-56° C. and solidifying at 52°-51° C.

In view of the results obtained in the renewed investigation of isoöleic acid it is very likely that isoerucic acid also will be found to consist of a complicated mixture of isomeric erucic acids.

Bromine in acetic acid solution yields dibromo-behenic acid which on treatment with alcoholic potash at 130°-140° C. is converted into behenolic acid, $CH_3(CH_2)_7.C{:}C.(CH_2)_{11}COOH$. On heating "isoerucic" acid with nitric acid, specific gravity 1·4, nonylic and brassidic acids, together with a small quantity of dinitrononane, are obtained.

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[1] *Gazz. chim. ital.*, 1910, II. 435 (2nd fascicle of that year).

[2] G. Goldschmidt, *Sitzungsb. d. K. K. Akad. d. Wissensch.*, 1876 (72), ii. 366.

[3] Alexandroff and N. Saytzeff, *Journ. f. prakt. Chem.*, 1894 (49), 58; Saytzeff, *ibid.*, 1894 (50), 65.

[4] *Gazz. chim. ital.*, 1904 (34), ii. 50.

[5] *Journ. f. prakt. Chem.*, 1892 (45), 301.

III.—ACIDS OF THE SERIES $C_nH_{2n-4}O_2$

(a) *Open Chain Acids*

(α) Acids of the Linolic Series

The acids belonging to this series are characterised by their power of absorbing four atoms of halogen or two molecules of iodochloride. According to *Molinari*,[1] they assimilate two molecules of ozone.[2] Hence these acids may be looked upon as containing two pairs of doubly-linked carbon atoms. Hydrogen in the presence of a catalyst reduces them to saturated acids. They readily absorb oxygen on exposure to the air; this important property is made use of in the arts (*drying oils*). By oxidation with potassium permanganate solution in the cold they yield tetrahydroxylated acids (see p. 232).

Nitrous acid does not convert them into solid isomerides. (Difference from oleic and erucic acids.)

The lead salts of these acids, like those of the oleic series, are soluble in ether. The barium salts are readily soluble in ether containing a small proportion of alcohol (cp. Chap. VIII. Difference from acids of the oleic series).

LINOLIC ACID, $C_{18}H_{32}O_2$[3]

Linolic acid occurs in considerable proportions in drying and semi-drying oils, and is most readily obtained from poppy seed, soya bean, maize, cotton seed, and sesamé oils, by brominating their mixed fatty acids, preparing, by recrystallising from petroleum ether, the tetrabromide of melting point 114° in a pure state, and reducing the latter with zinc and a methylalcoholic solution of hydrochloric acid. The methylester of linolic acid thus obtained is saponified in the cold with alcoholic soda or potash, and linolic acid is liberated from the soap by acidulating with a mineral acid (*Rollett*). The acid is finally purified by distillation *in vacuo*. Recent investigations have shown that a large number of non-drying oils (almond, arachis, olive), and even solid fats (hare fat, horse fat, lard) contain notable quantities of linolic acid.

Reformatzky[4] claimed to have prepared the pure acid by hydrolysing pure ethyl linolate; his "linolic" acid consisted, however, of a mixture of the unsaturated linseed oil acids (cp. "Linseed Oil," Vol. II. Chap. XIV.).

Linolic acid is a water-white oily liquid, which remains fluid at a temperature of $-18°$ C.; d^{18} C. $= 0{\cdot}9026$; boiling point 229°-230° C.

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[1] *Berichte*, 1908, 585; 2782.

[2] Cp. also Thieme, *Inaug. Dissert.*, Kiel, 1906.

[3] Goldsobel (*Journ. Russ. Phys. Chem. Soc.*, 1906 (38), 182) is of the opinion that the formula $CH_3(CH_2)_4.CH=CH.CH_2.CH=CH.(CH_2)_7.COOH$ probably represents best the constitution of linolic acid, and finds confirmation (*ibid.*, 1910 (42), 55) in the optical properties, a second possible formula $CH_3.(CH_2)_5.CH=CH.CH=CH(CH_2)_7.COOH$ requiring higher molecular refraction and dispersion than was actually found for his "linolic" acid. These deductions lose, however, their weight in view of the fact that "linolic" acid is most likely a mixture of two linolic acids.

[4] *Journ. Soc. Chem. Ind.*, 1890, 744.

under 16 mm. pressure, and 228° under 14 mm. pressure. It has a slightly acid reaction, and dissolves readily in alcohol and in ether. Nitrous acid does not produce a solid isomeride (important difference from oleic acid). Linolic acid absorbs oxygen rapidly from the atmosphere; when exposed to the air in a thin film it is converted into a solid resinous substance within a few days; after more prolonged exposure it forms a neutral body (frequently described as "linoxyn"[1]), insoluble in ether.

Linolic acid dissolves readily in concentrated sulphuric acid; the resulting sulpho-compound is insoluble in petroleum ether.[2] The product formed by the interaction of equal molecules of linolic and sulphuric acids leads to the addition of two molecules of sulphuric acid to one molecule of linolic acid, so that half of the linolic acid remains intact (*H. Schoenfeld*[3]), much as on treating linolic acid with one molecule of bromine no dibromide is obtained, one-half of the linolic acid yielding tetrabromide.

On brominating linolic acid with two molecules (4 atoms) of bromine in ethereal or chloroformic solution the **crystalline tetrabromide** $C_{18}H_{32}O_2Br_4$, melting at 114°-115° C. (*Hazura*); 114° C. (*Lewkowitsch*); 113°-114° C. (*Farnsteiner*) separates out. Excess of bromine does not produce the hexabromostearic acid obtainable from linolenic acid (p. 207); a certain quantity of linolic acid is, however, converted into another bromide, soluble in petroleum ether at the ordinary temperature.[4] At a higher temperature more of the liquid tetrabromide appears to be formed.

Bedford[5] therefore expressed the opinion that there exist two linolic acids, which he differentiates as α-linolic and β-linolic acids; of these α-linolic acid yields the solid bromo-derivative, whereas β-linolic acid yields a liquid bromo-derivative (cp. Vol. II. Chap. XIV. "Linseed Oil"). But the experimental proof for this assertion is wanting. *Rollett*[6] obtained from pure linolic acid in several experiments an amount of crystalline tetrabromide not exceeding 50 per cent of the theoretical yield, the remainder forming a liquid tetrabromide; from the latter a linolic acid can be obtained by reduction which yields again the crystallised tetrabromide, melting at 113°-114°, but only to the extent of 26 per cent of the theoretical quantity. Hence *Rollett* rejects the view that two isomeric linolic acids exist, and rather favours the view, that on brominating linolic acid two stereo-isomeric bromides are formed, each of which should represent a racemic compound, resolvable into optically active enantiomorphous substances.

These views are hotly contested by *Erdmann and Bedford*; more, however, on the strength of their objections to *Rollett's* theory in connection with linolenic acid than on the strength of experimental evidence. The results obtained by oxidising "linolic acid" would, however, point to the existence of two isomeric linolic acids in the "linolic" acid obtained from linseed oil (see below).

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[1] *Ibid.*, 1888, 680.

[2] Twitchell, *ibid.*, 1897, 1004.

[3] *Inaug. Dissert.*, Zürich, 1912.

[4] Cp. Reformatzky, *Journ. f. prakt. Chem.*, 1890 (41), 529; Hazura, *Monatsh. f. Chem.*, 1888 (9), 180; Rollett, *Zeit. f. physiol. Chem.*, 1909 (62), 410.

[5] *Inaug. Dissert.*, Halle a/S., 1906. Cp. also Fokin, *Zeits. f. Elektrochem.*, 1906, 759.

[6] *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1909, 410; 421.

The *crystalline tetrabromide*, melting at 114° C., is easily soluble in ether, alcohol, benzene, chloroform, and glacial acetic acid, but is sparingly soluble in petroleum ether (important difference from oleic acid, cp. Chap. VIII.). By treatment with zinc and alcoholic hydrochloric acid it is reduced to linolic acid.

The *liquid tetrabromide* is readily soluble in petroleum ether, for even after the removal of the bulk of the petroleum ether no crystalline compound separates out. *Matthes and Boltze*,[1] however, succeeded in obtaining silky scales, melting at 54°-55° C., by evaporating the petroleum ether solution of the liquid tetrabromide to dryness and recrystallising the residue from methyl alcohol. After recrystallisation from absolute alcohol these crystals have the constant melting point 57°-58° C. It would appear that *Farnsteiner*[2] had obtained already indications of this crystalline compound (cp. "Telfairic Acid," p. 200).

On oxidising linolic acid with a dilute solution of potassium permanganate in the cold, *Hazura* obtained tetrahydroxystearic (sativic) acid, $C_{18}H_{36}O_6$ (cp. p. 232). *Rollett*[3] obtained on oxidising pure linolic acid 40·7 per cent of tetrahydroxy acid, melting at 155° C. After recrystallising six times from alcohol, the melting point was still 156°-169°. By boiling the substance with 50 parts of benzene, whereby a very small quantity of a foreign substance was extracted, and afterwards recrystallising from alcohol, sativic acid, melting at 171°-173° C. was obtained. It would thus appear that two isomeric tetrahydroxystearic acids, the existence of which has been shown by *H. Meyer and R. Beer* (see p. 233), had been obtained from one and the same linolic acid.

Peters and Reformatzky claim to have obtained stearic acid by heating "linolic acid" with phosphorus and hydriodic acid to 200° C. In view of *Goldschmidt's* experiments with oleic and erucic acids under the same conditions, no doubt need be entertained as to these observers having actually obtained stearic acid. (The linolenic acid which their raw material contained would also have yielded stearic acid.)

Linolic acid is readily reduced to stearic acid by hydrogen in the presence of a catalyst.

Ammonium linolate melts at 57°-58° C.; it is easily soluble in methylalcohol, carbon bisulphide, carbon tetrachloride, chloroform, and warm benzene and acetone; sparingly soluble in ether (*Falciola*).[4]

Potassium linolate, $C_{18}H_{31}O_2K$, forms a white crystalline mass easily soluble in alcohol, less readily soluble in water. On exposure to the air the salt becomes rapidly yellow; above 200° C. it turns dark brown with decomposition (*H. Schoenfeld*).[5]

The potassium salt of the tetrabromide, $C_{18}H_{31}Br_4O_2K$, forms a white crystalline powder, melting at 171° C., easily soluble in alcohol, sparingly soluble in water.

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[1] *Arch. d. Pharm.*, 1912 (250), 225.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1899, 19.

[3] *Zeits. f. physiol. Chem.*, 1909, 421.

[4] *Gazz. chim. ital.*, 1910, ii. 431.

[5] *Inaug. Dissert.*, Zürich, 1912.

The metallic salts of "linolic acid" are amorphous, with the exception of the *zinc* salt. *Barium* and *calcium linolates* are soluble in boiling alcohol. The *calcium, barium, zinc, copper*, and *lead* salts dissolve in ether. *Barium linolate* is easily soluble in benzene and petroleum ether (important difference from barium oleate). The *lead* salt of the tetrabromide melting at 114° C., is sparingly soluble in cold ether and in benzene; it dissolves easily in a mixture of two parts of benzene and one part of alcohol in the hot, and separates out in crystals on cooling. Linolates absorb oxygen more readily than does the free acid (cp. "Driers," Vol. III. Chap. XV.).

Methylester, obtained from the crystalline tetrabromide by treatment with granulated zinc and methyl alcohol containing hydrochloric acid gas (one tenth normal acid), distils at 221°-224° C. under a pressure of 35 mm., at 211°-212° C. under 16 mm., and at 207°-208° C. under 11 mm. pressure. $d_4^{18} = 0{\cdot}8886$. Iodine value 172·3 (theory 172·8).

For other isomerides of linolic acid, obtained by the action of heat on ricinoleic and ricinelaïdic acids respectively, see pp. 214, 220.

MILLET OIL ACID, $C_{18}H_{32}O_2$

The individuality of this acid, which is assumed by *Kassner*[1] to occur as a glyceride in millet seed oil (see Vol. II., "Millet Seed Oil"), is doubtful.

TELFAIRIC ACID, $C_{18}H_{32}O_2$

This acid occurs in koeme oil;[2] and has been isolated by fractional distillation of its liquid fatty acids. It solidifies at 6° C. and boils at 220°-225° C. under a pressure of 13 mm. By oxidation with potassium permanganate in dilute alkaline solution at 0° C. a tetrahydroxystearic acid, melting at 177° C., is obtained. Its tetrabromide melts at 57°-58° C.

This melting point coincides with that of the tetrabromide described above (p. 199) under the heading of *liquid tetrabromide*, and suggests identity of the products.

ELÆOMARGARIC ACID, ELÆOSTEARIC ACID, $C_{18}H_{32}O_2$

Elæomargaric acid occurs in tung oil (Chinese, and Japanese wood oil) and crystallises in rhombic plates melting at 48° C. (*Cloëz, Maquenne*), 43·8° C. (*de Negri and Sburlati*), 43°-44° C. (*Kametaka*). It readily absorbs oxygen from the atmosphere and is thereby converted into a resinous mass.[3] In an alcoholic (or ethereal) solution the acid remains unchanged if protected from light; on exposure to light, however, crystals melting at 71° C. are deposited from the solution. These crystals have the same composition as elæomargaric acid. According to *Maquenne*,[1] the higher melting acid, termed by *Cloëz* elæostearic acid, is a stereometric isomeride of elæomargaric acid, and stands to it in the same relationship as does elaïdic acid to oleic acid. *Maquenne* ascertained that the elæomargaric acid to which *Cloëz* had ascribed the formula $C_{17}H_{30}O_2$, contained 18 carbon atoms and assigned to it the formula $C_{18}H_{30}O_2$. He proposed to term "elæomargaric acid" "α-elæostearic acid," assigning to the isomeride melting at 71° C. the name β-elæostearic acid.

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[1] *Journ. Chem. Soc.*, 1888, Abstr. 673. *Arch. d. Pharm.* 225, 1081.

[2] Thomas, *Arch. d. Pharm.*, 1900, 238, 48.

[3] Cp. Kitt. *Chem. Revue*, 1904, 1190.

The author has not adopted the name elæostearic acid, as it was found in his laboratory[2] that the composition as expressed by the formula $C_{18}H_{30}O_2$ must be incorrect, inasmuch as no ether-insoluble bromide could be obtained from tung oil. Later on, *Kametaka*[3] showed that the true composition of the acid is $C_{18}H_{32}O_2$. The acid must be considered a stereoisomeride of linolic acid, since on bromination it yields a tetrabromide, identical with the crystalline tetrabromide obtained from linolic acid.

On oxidising elæomargaric acid with potassium permanganate *Kametaka*[4] obtained dihydroxystearic acid, azelaïc acid, and an unknown crystalline-substance melting at 123°-125° C., soluble in water and alcohol, but insoluble in ether. Sativic acid was not found; in *Kametaka's* opinion this is probably due to the temperature during oxidation having been too high, the sativic acid at first formed having been further oxidised to azelaïc acid.

Treatment of elæomargaric acid with five times its weight of concentrated sulphuric acid yielded no definite products. As this behaviour differs from that of behenolic and stearolic acids, which contain trebly-linked carbon atoms, *Kametaka* draws the conclusion that elæomargaric acid contains no triple bond.

A more recent examination by *Majima* confirmed the composition $C_{18}H_{32}O_2$, and therefore the name "elæostearic" may be acceptable. The "elæostearic" acid, prepared by *Majima*, following *Kametaka's* directions, melted at 48°-49° C., and boiled under 12 mm. pressure in an atmosphere of carbon dioxide at a temperature of 235° C.

Elæostearic acid, treated in chloroform solution with ozonised air at 0° C. until bromine is no longer assimilated, absorbs two molecules of ozone (*Majima*[5]) yielding the ozonide $C_{18}H_{32}O_8$. This ozonide is decomposed, by boiling with water, into *n*-valeraldehyde, normal valeric acid, the semi-aldehyde of azelaïc acid, and azelaïc acid. The conclusion derived therefrom that elæostearic acid has the constitution $CH_3(CH_2)_3CH=CH.(CH_2)_2CH=CH(CH_2)_7.COOH$ is, however, no longer maintained by *Majima*.[6] By reducing elæostearic acid by means of an electric current, *Fokin*[7] obtained stearic acid. This acid was obtained in quantitative yield by catalytic reduction (*Majima and Okada*).[6]

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[1] *Compt. rend.*, 1902 (135), 696.

[2] Walker and Warburton, *Analyst*, 1902, 237.

[3] *Journ. Chem. Soc.*, 1903, 1042.

[4] *Journ. Coll. Scien. Imp. Univ. Tokyo*, 1908 (25), Art. 3.

[5] *Berichte*, 1909, 674.

[6] *Ibid.*, 1912, 2730. Cp. also R. S. Morrell, *Journ. Chem. Soc.*, 1912, 2083.

[7] *Zeits. f. Elektrochem.*, 1906, 759.

Fokin[1] recently proposed the following constitutional formula for elæostearic acid :—

$$CH_3.(CH_2)_3.CH=CH.CH=(CH_2)_9COOH$$

Methylester, decomposes on warming, becoming dark coloured and giving off a disagreeable odour.

Ethylester, distils at 230°-240° C. under a pressure of 25 mm.

(β) Acids of the Tariric Series.

Acids belonging to this series are isomeric with those of the linolic series, but differ most essentially from them by containing one triple bond. Hitherto only one representative of this series has been found in nature, viz. tariric acid.

This acid absorbs four atoms of bromine to form a saturated acid. The formation of a di-iodide is only effected by agitating with iodine in a solution of glacial acetic acid at 50° or 60° C. ; a tetra-iodo addition product could, however, not be obtained. With *Hübl's* solution only one molecule of iodo-chloride is absorbed. This appears to be a characteristic property of fatty acids having a triple bond, and would seem to allow to distinguish them chemically from the isomeric linolic acids having two double bonds. In this and in other respects tariric acid simulates completely the acids of the "stearolic series," which are dealt with separately, as they are not found in nature.

The question whether tariric acid is identical with stearolic acid, is denied by *Grützner*[2] not only on account of the difference in their melting points (stearolic acid melts at 48° C.), but also because of the difference of their bromo-derivatives and of the solubilities of their respective salts. *Arnaud and Hasenfratz* also deny the identity of stearolic acid with tariric acid, as the former yields on oxidation (with nitric acid), pelargonic and azelaïc acid, whereas tariric acid leads to lauric and adipic acids.

TARIRIC ACID, $C_{18}H_{32}O_2=CH_3.(CH_2)_{10}C\equiv C(CH_2)_4.COOH$

Tariric acid has been found[3] in the oil from the seeds of the Guatemalan "Tariri," *Picramnia Sow*, Aublet, in the oil from *Picramnia Camboita*, Engl.,[4] and in the oil from *Picramnia Lindeniana*, Tulasne. In the last-named oil it occurs to the extent of 20 per cent.[5] It melts at 50·5° C. and absorbs four atoms of bromine ; the tetrabromide melts at 125° C. The dibromide of tariric acid, $C_{18}H_{32}Br_2O_2$, melts at 32° C. (*Arnaud*,[6] *Grützner*).

By reduction of tariric acid with hydriodic acid and amorphous phosphorus, stearic acid[3] is obtained. By oxidation with fuming nitric acid, lauric and adipic acids are formed. Hence *Arnaud*[1] ascribes to tariric acid the above given constitutional formula.

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[1] *Journ. Russ. Phys. Chem. Soc.*, 1913 (45), 283.

[2] Grützner, *Chem. Zeit.*, 1893, 879, 1851.

[3] *Compt. rend.*, 1892 (114), 79.

[4] Grutzner, *Chem. Zeit.*, 1893, 879, 1851.

[5] Grimme, *Chem. Rev.*, 1912, 51.

[6] Arnaud, *Compt. rend.*, 1896 (122), 1000.

By oxidation with potassium permanganate *Arnaud and Hasenfratz* obtained lauric and glutaric acids on the one hand and undecylic and adipic acids on the other, the proportion of the two groups of oxidation products being approximately of 4 : 1. By carefully regulated oxidation the diketonic acid—taroxylic acid—$CH_3.(CH_2)_{10}.CO - CO.(CH_2)_4COOH$, is obtained.

The *potassium* salt is only slightly soluble in 98 per cent alcohol, 100 parts of the latter dissolving 2·48 parts at 15° C.

The *barium* salt is amorphous and remains stable up to 180° C.; it is very slightly soluble in boiling alcohol.

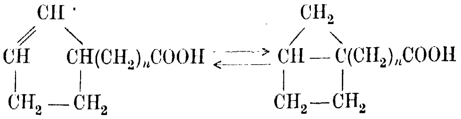
The *silver* salt crystallises in fine needles.

Tariric di-iodide, $C_{18}H_{32}I_2O_2$, is obtained by allowing the theoretical quantity of iodine to act on a solution of tariric acid in glacial acetic acid solution. It crystallises (from alcohol) in fine colourless needles, melting at 48·5° C. The ammonium salt crystallises in long hard needles which are slightly soluble in cold alcohol (difference from di-iodo-stearolic acid). By reduction with zinc and hydrochloric acid, the iodine is easily removed with regeneration of the original tariric acid (*Arnaud and Posternak*[2]).

Tariric monohydriodide, is obtained by passing one molecule of hydriodic acid through melted tariric acid. By reduction with zinc and glacial acetic acid it yields tarelaïdic acid[3] (cp. above).

(*b*) *Cyclic Acids—Acids of the Chaulmoogric Series*

The acids belonging to this group differ from the "open chain acids" in that they are cyclic compounds, and therefore contain only one pair of doubly-linked carbon atoms. In accordance therewith, they absorb two atoms of bromine or iodine. From an exhaustive study of these acids, especially of their oxidation products (see below), *Barrowcliff and Power*[4] arrive at the conclusion that the constitution of these acids must be expressed by the following tautomeric formulæ:—



which may be summarised by the following formula, in which the dotted lines indicate the state of equilibrium between one hydrogen atom and two carbon atoms:—

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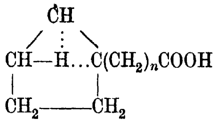
[1] Arnaud, *Compt. rend.*, 1902 (134), 473, 842; cp. also Arnaud and Hasenfratz. *Ibid.*, 1911 (152), 1603.

[2] *Compt. rend.*, 1909 (149), 220; French patent 407,412; English patent 24,721, 1909; U.S.A. Pat. 982,656; Arnaud and Posternak, F. Hoffmann—La Roche and Co.

[3] Arnaud and Posternak, *Compt. rend.*, 1910 (150), 1130.

[4] *Journ. Chem. Soc.*, 1907, 577.



These acids are remarkable on account of their property of rotating the plane of polarised light. Several homologues belonging to this series exist in chaulmoogra, hydnocarpus, and lukrabo oils (see Vol. II. Chap. XIV. "Chaulmoogra Oil Group"). Hitherto only the two following homologues have been prepared in a pure state.

HYDNOCARPIC ACID,[1] $C_{16}H_{28}O_2$

Hydnocarpic acid was isolated from the mixed fatty acids of hydnocarpus oil by crystallisation from alcohol. The acid also occurs in chaulmoogra and lukrabo oils in association with chaulmoogric acid. It crystallises (from alcohol) in the form of lustrous leaflets, melting at 59°-60° C., sparingly soluble in the usual organic solvents in the cold, with the exception of chloroform, which dissolves the acid easily. $[\alpha]_D = +68{\cdot}1°$. Like chaulmoogric acid, it undergoes a change on keeping, acquiring a yellow colour; at the same time the melting point is lowered. If it be then distilled under diminished pressure, a brown resinous substance is left in the distilling flask. This change takes place more readily with hydnocarpic acid than with chaulmoogric acid.

On oxidation in alkaline solution with an excess of potassium permanganate, there are obtained: *n*-decanedicarboxylic acid $(CH_2)_{10}(COOH)_2$ and a tricarboxylic acid melting at 60° C., most likely having the constitution of a *n*-tridecane-$\alpha\alpha'\gamma$-tricarboxylic acid, $CO_2H.(CH_2)_2CH.(COOH)[CH_2]_{10}CO_2H$. Hydnocarpic acid is not attacked by melted potassium hydrate, even at 250° C. The aqueous solution of the sodium salt is at once decolourised by potassium permanganate in the cold.

Methylester, colourless oil, boiling at 200°-203° C., solidifying to colourless crystals, melting at 8° C. $[\alpha]_D = +51{\cdot}6°$.

CHAULMOOGRIC ACID, $C_{18}H_{32}O_2$

This acid[2] occurs in chaulmoogra, hydnocarpus, and lukrabo oils. It is obtained from the mixed fatty acids of chaulmoogra oil by crystallisation from petroleum ether, followed by distillation under diminished pressure and recrystallisation from alcohol. It crystallises in colourless glistening leaflets, melting at 68° C. when freshly distilled, and boiling at 247°-248° C. under a pressure of 20 mm. $[\alpha]_D = +62{\cdot}1°$ in chloroformic solution.[3] After keeping for some time the specific rotation somewhat diminishes and the acid acquires a yellowish colour. If it be then again distilled, a dark brown substance is left in the distilling flask.

[1] Power and Barrowcliff, *ibid.*, 1905, 895; Barrowcliff and Power, *ibid.*, 1907 577.

[2] Power and Gornall, *Journ. Chem. Soc.*, 1904, 853.

[3] Barrowcliff and Power, *ibid.*, 1907, 565.

On treating chaulmoogric acid with hydrobromic acid in glacial acetic acid, bromodihydrochaulmoogric acid, $C_{18}H_{33}BrO_2$ (melting at 36°-38° C.) is formed. This acid is optically inactive. By reducing chaulmoogric acid with zinc dust and alcohol, dihydrochaulmoogric acid, $C_{18}H_{34}O_2$ (melting at 71°-72° C., and boiling at 248° C. under a pressure of 20 mm.), is formed. This is a saturated acid, and is also optically inactive. The same acid is obtained by treating chaulmoogric acid with hydriodic acid and phosphorus, a hydrocarbon chaulmoogrene, $C_{18}H_{34}$ (boiling at 193°-194° C. under 200 mm. pressure), being obtained as a by-product. Chaulmoogric acid is not attacked by fused caustic alkalis, even at 300° C. On oxidising chaulmoogric acid in the cold with an alkaline solution of potassium permanganate equivalent to two or three atomic proportions, two isomeric acids are formed: α-dihydroxydihydrochaulmoogric acid (melting at 105° C.; $[\alpha]_D = +11{\cdot}6°$), and β-dihydroxydihydrochaulmoogric acid (melting at 93° C.; $[\alpha]_D = -14{\cdot}2°$), at the same time formic acid is produced. On oxidising chaulmoogric acid with an excess of potassium permanganate in alkaline solution a tricarboxylic acid, $C_{18}H_{32}O_6$, melting at 68° C., is obtained, together with n-dodecanedicarboxylic acid, $[CH_2]_{12}(CO_2H)_2$, a smaller quantity of a n-undecanedicarboxylic acid, $[CH_2]_{11}(CO_2H)_2$, and still smaller quantities of oxalic and malonic acids.

On allowing sodium to act on chaulmoogric acid in amyl alcohol solution in the hot, chaulmoogryl alcohol, $C_{18}H_{33}OH$ (melting-point 36° C.; $[\alpha]_D = +38{\cdot}4°$) and chaulmoogryl chaulmoograte, $C_{17}H_{31}.CO_2.C_{18}H_{33}$ (melting point 42° C.) are obtained, together with unchanged chaulmoogric acid.

Methylester, melts at 22° C., boils at 227° C. (corr.) under a pressure of 20 mm.; $d_{25}^{25} = 0{\cdot}9119$; $[\alpha]_D^{15} = +50°$ in chloroformic solution.

Ethylester, a colourless oil, boiling at 230° C., under a pressure of 20 mm.; $d_{16}^{15} = 0{\cdot}9079$; $[\alpha]_D^{20} = +50{\cdot}7°$.

IV.—ACIDS OF THE LINOLENIC SERIES $C_nH_{2n-6}O_2$

The acids of this series assimilate six atoms of bromine, or three molecules of iodochloride. This might be due to the presence of two pairs of trebly linked, or of three pairs of doubly linked carbon atoms. Since linolenic acid absorbs three molecules of ozone (*Molinari*), it may be assumed to contain three pairs of doubly linked carbon atoms. Linolenic acid can be reduced to stearic acid; hence a straight chain of eighteen carbon atoms must occur in the molecule.

These acids readily absorb oxygen from the air, a property of which extensive use is made in the arts (*drying oils*).

The *lead* and *barium* salts are easily soluble in ether. Nitrous acid does not yield solid isomerides. With regard to the separation of these acids from those of the other series of unsaturated acids, see Chap. VIII.

LINOLENIC ACID, $C_{18}H_{30}O_2$ [1]

Linolenic acid occurs in notable quantities in all vegetable drying oils, especially in linseed oil (cp. Vol. II. Chap. XIV. " Drying Oils "). The acid was first prepared by *Hazura*,[2] from the crystalline hexabromide[3] obtained by brominating the mixed liquid acids of linseed oil (cp. Chap. VIII.). This hexabromide (see description below), yields linolenic acid by reduction with zinc and alcoholic hydrochloric acid. The acid obtained by *Hehner and Mitchell*[4] was a nearly colourless oil, of the specific gravity 0·9228 at 15·5° C. (water at 15·5° C. = 1), and is stated to have a fishy odour. *Bedford* prepared it by boiling the hexabromide with alcohol and rasped zinc (whereby the bromine is removed in about one hour). This acid was an almost colourless oil of a faint, but not unpleasant smell (not recalling that of fish); it was also prepared by the reduction of the ethylester of hexabromo-linolenic acid (see below). It distilled *in vacuo* (0·001 to 0·002 mm. pressure, rise of vapours above the liquid 75 mm.) at 157°-158° C. without undergoing decomposition. Linolenic acid, prepared by *Rollett*[5] by saponification of the methylester boiled between 230° and 232° C. at 17 mm. pressure, and had $d^{18}_{4} = 0{\cdot}9141$.

Erdmann and Bedford[6] assume the existence of two linolenic acids, which they differentiate as α- and β-linolenic acids. In their view α-linolenic acid is the acid occurring in linseed oil, and yielding quantitatively the crystalline hexabromide melting at 180° C. Since the " linolenic acid " from this hexabromide yields, on rebromination, only 23 per cent of the original hexabromide, *Erdmann and Bedford* assume that the remaining 77 per cent consist of a " β-linolenic " acid, a liquid acid, which was assumed to absorb four atoms of bromine only. (This liquid tetrabromide had been looked upon by *Hazura* as an ether-soluble " isolinolenic hexabromide ".)

Erdmann, Bedford, and Raspe,[7] regarded as a confirmation of their theoretical views the fact, that the " linolenic " acid obtained by the reduction of the crystalline hexabromide yields two linolenic-acid-ozonides, $C_{18}H_{30}O_{11}$, which could be differentiated from each other by the velocity with which they are decomposed by water. That ozonide which is decomposed at the ordinary temperature is looked upon by them as a derivative of α-linolenic acid.

Both linolenic acids are, therefore, in the opinion of *Erdmann, Bedford, and Raspe*, stereoisomerides, and thus simulate, as regards their constitution, oleic and elaïdic acids respectively.

In the author's opinion, however, no decisive value can be ascribed to these facts, for they are, as a proof, of the same order and value as that derived from the bromides.

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[1] Goldsobel (*Journ. Russ. Phys. Chem. Soc.*, 1910 (42), 55), suggests the constitutional formula $CH(C_2H_5)=CH.CH_2.CH=CH.CH_2.CH=CH.(CH_2)_7COOH$.

[2] *Journ. Soc. Chem. Ind.*, 1888, 506.

[3] Cp. O. Süssenguth, *Zeits. f. phys. Chem.*, 1865, 563. For the conflicting statements published in the older literature of this subject, cp. the 4th edition of this work, 1909, Vol. I. p. 160.

[4] *Analyst*, 1898, 313.

[5] *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1909 (62), 424.

[6] *Berichte*, 1909, 1328; 1334. *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1910 (68), 76; Erdmann, *ibid.*, 1911 (74), 180.

[7] *Berichte*, 1909, 1334.

Rollett[1] rejecting the view that β-linolenic acid is a chemical individual, explains the fact that only about 23 per cent of hexabromide are obtained from linolenic acid prepared by reduction of the crystalline hexabromide, by assuming that on brominating linolenic acid, four different bromo-addition products can be obtained (each of which can be resolved into two optically active isomerides). If, then, only one isomeride is crystalline, the yield of 23 per cent would be readily explained. Moreover, *Rollett* showed that the liquid tetrabromide, considered to be a derivative of β-linolenic acid, is still an unsaturated substance, which absorbs more bromine, finally yielding a hexabromo derivative (see also above). Nothing being known as to the properties of β-linolenic acid and the occurrence of β-linolenic in linseed oil not being established, the existence of the β-linolenic acid must be considered as hypothetical. (For the controversial papers published by *Erdmann and Bedford* on the one hand and *Rollett* on the other, the reader must be referred to the originals and to the critical summaries given by the author[2] in the *Jahrbuch der Chemie.*)

The properties of α-linolenic acid as probably representing the purest acid prepared hitherto, are given here according to *Erdmann's* statements.

α-Linolenic acid, prepared from its zinc salt (see below) is, at the ordinary temperature, a water-white mobile liquid, soluble in 10 parts of petroleum ether; when this solution is cooled to a low temperature, the acid separates in the form of a white solid precipitate. It is also soluble in alcohol and ether. $d_4^{20} = 0{\cdot}9046$ (another preparation a few days old and, hence, undoubtedly oxidised gave $d_4^{21} = 0{\cdot}9248$). On standing the acid becomes oxidised easily, whilst the specific gravity rises and the iodine value, of course, falls.

In *Erdmann's* opinion the increase of the density may be also due to polymerisation; this, however, must be left an open question as the proof adduced for this opinion so far would seem to require further support.

On brominating the liquid linseed oil fatty acids a crystalline hexabromide, melting at 180°-182° (*Hehner and Mitchell*; *Rollett*), 180°-181°; 183° (*Lewkowitsch*), 179°-180° (*Bedford*), is obtained.[3] It has been pointed out already that on reducing this hexabromide and re-brominating it, only about 23 per cent of the theoretically possible hexabromide are recovered. *Rollett's* theoretical explanation has been given above. The α-linolenic acid obtained by *Erdmann* from linseed oil linolenic acid by purification through the zinc salt gave, on bromination, the full theoretical yield of hexabromide melting at 180° C. It would seem necessary to complete the chain of evidence based on this fact by *Erdmann*, by reducing the hexabromide thus obtained to linolenic acid, again brominate it and determine the yield.

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[1] *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1909 (62), 410; *ibid.*, 1910 (70), 404.

[2] XIX., 434; XX., 420; XXI., 445.

[3] Eibner and Muggenthaler (*Farbenzeitung*, 1912, 131 and ff.) consider 177° as the correct melting point (see Chap. VIII.).

In the filtrate from the insoluble hexabromide, a liquid bromide is found, which was looked upon by *Hazura* as the ether-soluble "isolinolenic hexabromide."

This liquid bromide appeared to *Erdmann and Bedford* to be a tetrabromide, and thus seemed to confirm the view that α and β linolenic acid did exist. *Rollett*, however, showed that this hypothetical tetrabromide still absorbed bromine, finally yielding a liquid hexabromide.

In view of the importance attaching to the behaviour of the crystalline hexabromide, the following derivatives of "α-linolenic" acid are described:—

Potassium hexabromo linolenate, separates from a hot mixture of benzene and alcohol as a crystalline white powder (*Bedford*).

Barium hexabromo linolenate, obtained by shaking hexabromo-α-linolenic acid with an excess of baryta solution (*Bedford*).

Methylester, melting point 157°-158° C. (*Bedford*).

Ethylester, melting point 151·5°-152·5° C. The ester can be obtained by brominating the ethylester of "α-linolenic" acid (*Bedford*).

Trichloro-triiodo-stearic acid, $C_{18}H_{30}O_2Cl_3J_3$, obtained from α-linolenic acid and iodomonochloride forms colourless crystals melting at 146° C. The acid can be prepared direct from crude linseed oil fatty acids by cooling them to $-18°$ C., removing the solid fatty acids and treating the filtrate with iodomonochloride in glacial acetic acid solution (*Erdmann*).

Tribromo-triiodo-stearic acid, $C_{18}H_{30}O_2Br_3J_3$, prepared from crude linseed oil fatty acids and iodomonobromide forms crystals melting at 124°-126° C. By shaking with lime water the *calcium* salt, $(C_{18}H_{29}O_2Br_3J_3)_2Ca$, is obtained (*Erdmann*).

The statement made by *Peters* and by *Reformatzky*, that linolenic acid can be reduced by fuming hydriodic acid and red phosphorus to stearic acid, although it could not be confirmed by *Bedford*, need not be doubted in view of *Goldschmidt's* experiments with oleic and erucic acids, as both linolic and linolenic acid contained in the linseed oil fatty acids, with which *Peters* and *Reformatzky* worked, would yield stearic acid. Linolenic acid is, however, converted quantitatively into stearic acid by reducing it with hydrogen in the presence of finely distributed nickel (cp. Vol. III. Chap. XV. "Conversion of Oleic Acid into Stearic Acid").

Linolenic acid absorbs oxygen rapidly from the atmosphere and acquires thereby a dark brown colour. It absorbs 3 molecules of ozone forming well-defined ozonides. Two ozonides obtained by *Erdmann, Bedford, and Raspe* have been mentioned above. On decomposition with water both ozonides yield the same products, viz. propionic aldehyde, malonic acid, and the aldehydes of malonic and azelaïc acids.

By oxidation with an alkaline solution of potassium permanganate in the cold, *Hazura* obtained two hexa-hydroxystearic acids, termed by him linusic and isolinusic acids respectively. This result seemed to point to the existence of two isomeric linolenic acids. Since, however, *Rollett* has shown that by oxidation of the linolenic acid, obtained by reduction of the crystalline hexabromide, linusic acid as well as isolinusic acid are obtained, the evidence resting on the existence of two hexahydroxy acids becomes inconclusive, *Rollett's* (see above) theoretical views being equally capable of explaining the formation of two isomeric oxidation products.

The most important salt of linolenic acid (which served for the preparation of the pure acid) is the *basic zinc* salt $(C_{18}H_{29}O_2)_2Zn + \frac{1}{2}ZnO$, melting at 72°-73° C. 100 c.c. of an alcoholic solution saturated in the cold contained 0·8924 grm. of the salt; 100 c.c. of the solution saturated in the hot contained 6·170 g.

Methylester, obtained by reduction of the crystalline hexabromide with zinc in a methylalcoholic solution of hydrochloric acid gas (*Rollett*[1]). The ester boils at 207° C. under 14 mm. pressure; $d_4^{20} = 0{\cdot}8919$.

Ethylester, boils at 132°-133° C. under a pressure of 0·001 mm. $n_D^{20} = 1{\cdot}46753$. This ester was obtained by reducing the ethylester of hexabromolinolenic acid (*Bedford*). On reducing it with hydrogen in the presence of nickel, ethyl stearate is obtained. The ester furnishes on treatment with ozone in chloroform solution a perozonide (" α-perozonide ").[2]

The existence of *Isolinolenic acid*, $C_{18}H_{30}O_2$, was inferred by *Hazura*[3] from the fact that he obtained, on oxidising the mixed linseed oil acids with potassium permanganate, " isolinusic " acid (see p. 233) in addition to linusic acid. *Bedford* expressed the opinion that the oxidation product consisted of a complicated mixture of different substances which cannot be resolved into its several constituents (cp. " Isolinusic Acid "). Although the individuality of isolinusic acid has been established by other observers, *Rollett* shows that there is no reason for concluding therefrom that an isolinolenic acid does exist (see above).

JECORIC ACID, $C_{18}H_{30}O_2$

Fahrion[4] assumes the existence of this acid in sardine oil on the strength of analyses of the barium, calcium, and magnesium salts. Other analytical data, however, such as ultimate analysis, neutralisation number, and iodine value, do not agree with those required by theory. Nor does jecoric acid conform to *Hazura's* rule, inasmuch as it does not yield a hydroxylated acid on oxidation, volatile acids and carbon dioxide only being obtained. It appears to the author that this hypothetical acid is nothing else than impure clupanodonic acid (see p. 210).

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[1] *Hoppe-Seyler's Zeits. f. physiolog. Chem.*, 1909 (62), 423.

[2] Erdmann, Bedford, and Raspe, *Berichte*, 1909, 1336.

[3] *Journ. Soc. Chem. Ind.*, 1888, 506.

[4] *Ibid.*, 1893, 938.

V.—ACIDS OF THE SERIES $C_nH_{2n-8}O_2$. ACIDS OF THE CLUPANODONIC SERIES

ISANIC ACID, $C_{14}H_{20}O_2$

Isanic acid[1] is stated to occur, to the extent of about 10 per cent, in the oil from the seeds of I'Sano or Ungueko (a large tree of the *Oleaceæ* family, growing in the French Congo).

The acid was obtained in the form of foliated crystals (from ether) melting at 41° C., readily soluble in strong alcohol, ether, chloroform, benzene, acetone, methyl alcohol, and petroleum ether. Its odour is peculiarly characteristic of the seeds themselves. The acid is extremely susceptible to change of colour on exposure to air, turning thereby rose-red, the tinge deepening with the increased absorption of oxygen. The oxidised rose-coloured substance is insoluble in ether.

The existence of this acid is very doubtful, although its formula has been derived from analyses of the acid itself, as also of the silver and barium salts. The cryoscopic determination of the molecular weight gave 217 ($C_{14}H_{20}O_2 = 220$), but the acid absorbed only about 2 molecules of bromine. Reduction of the acid by means of hydriodic acid did not lead to conclusive results.

The existence of *therapic acid*, $C_{17}H_{26}O_2$, in cod liver oil (to the extent of 20 per cent) is inferred by *Heyerdahl*[2] from a bromine product, $C_{17}H_{26}Br_8O_2$, obtained on brominating the cod liver oil fatty acids. (The name was intended to express his opinion that the acid plays the most important part in the therapeutical effect of cod liver oil.) In the author's opinion therapic acid is identical with clupanodonic acid.

The therapic acid described by *Heiduschka* and *Rheinberger*[3] and its tetrachloro-tetrabromo and tetrachloro-tetraiodo derivatives are in the author's opinion nothing else than clupanodonic acid and its addition products respectively. The author[4] has pointed out that the analytical data agree better with an acid having 18 carbon atoms than, as claimed, an acid of 17 carbon atoms.

CLUPANODONIC ACID,[5] $C_{18}H_{28}O_2$

Clupanodonic acid (Japanese, *iwashi san*) has been obtained from its octobromide by reduction with zinc and alcoholic hydrochloric acid. The acid occurs in the mixed fatty acids from Japanese sardine oil, herring, whale (dab and green turtle) oils, and appears to be a characteristic constituent of all fish, liver, and blubber oils. It is a pale yellow liquid having a fishy smell. On exposure to the air it easily becomes oxidised, changing to a dry, varnish-like mass in the course of a few days. This mass is undoubtedly an "oxidised clupanodonic acid" which had been first observed by the author (see Vol. II. Chap. XIV. "Marine Animal Oils").

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[1] *Journ. Soc. Chem. Ind.*, 1896, 660.

[2] *Cod Liver Oil and Chemistry*, p. xcv.

[3] *Pharm. Zentralb.*, 1911, No. 32.

[4] *Jahrbuch d. Chemie.*, 1911, xxi. 445.

[5] M. Tsujimoto, *Journ. College of Eng.*, Tokyo Imp. Univ., 1906, vol. iv. No. 1, 1908, No. 5.

Clupanodonic octobromide, $C_{18}H_{28}O_2Br_8$, is obtained by brominating a glacial acetic acid solution of the mixed fatty acids of fish, liver, and blubber oils, and washing the precipitate with a large quantity of ether until the washings leave no residue. The bromide forms a white powder which turns slightly grey on drying at 100° C. It is very sparingly soluble in ether, alcohol, and glacial acetic acid, even in the hot, more readily soluble in hot benzene. It does not melt below 200° C. (difference from hexabromolinolenic acid). At this temperature it blackens, and on further heating is decomposed without melting.

In the author's opinion "jecoric" acid and "therapic" acid are nothing else than (impure) clupanodonic acid.

ARACHIDONIC ACID, $C_{20}H_{32}O_2$

The existence of an acid of this composition is inferred[1] from the formation of octobromoarachidic acid (see Chap. VIII.) and octohydroxy arachidic acid obtained respectively by the bromination and oxidation of the unsaturated fatty acids in liver lecithin. As *Hartley* has not named this acid the author suggests the term *arachidonic acid.*

Acids having the formulæ $C_{20}H_{32}O_2$ and $C_{24}H_{40}O_2$ are assumed by *Bull*[2] to occur in herring oil; *Tsujimoto*, however, was unable to identify them therein.

VI.—HYDROXYLATED ACIDS, $C_nH_{2n}O_3$

SABINIC ACID, $C_{12}H_{24}O_3 = CH_2(OH) - (CH_2)_{10}.COOH$

Sabinic acid occurs, together with juniperic acid, in the waxy substances obtained from the leaves of *Juniperus Sabina* (*Bougault and Bourdier*[3]). It has not been found in the waxy substances from the leaves of other coniferous plants (see p. 68). The separation from juniperic acid is based on the insolubility of the sodium salt of the latter in a four per cent salt solution (see p. 69). The acid dissolves very easily in alcohol. Acetone at 20° C. dissolves about 10 per cent. Sabinic acid is very sparingly soluble in cold petroleum ether, but readily soluble in the hot.

Acetyl sabinic acid, $C_{12}H_{22}(O.C_2H_3O)COOH$, melts at 43° C. It is easily soluble in ether, petroleum ether, in 90 per cent, and even 60 per cent alcohol. The sodium salt is soluble in a four per cent common salt solution, but is precipitated therefrom by the addition of considerable quantities of sodium chloride. The *barium, lead,* and *silver* salts are amorphous.

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[1] Hartley, *Journal of Physiology*, 1909 (38), 353.

[2] *Journ. Soc. Chem. Ind.*, 1900, 73; *Chem. Zeit.*, 1899, 906.

[3] *Compt. rend.*, 1908, 1311; 1910 (150), 875. *Journ. de Pharm. et de Chim.*, 1909 (30), 10.

JUNIPERIC ACID, $C_{16}H_{32}O_3 = CH_2(OH)-(CH_2)_{14}-COOH$

Juniperic acid occurs, according to *Bougault and Bourdier*,[1] as an "etholide" (see p. 69) in the waxy substance obtained from the leaves of coniferous plants (*Juniperus Sabina, J. communis, Picea excelsa, Pinus sylvestris, Thuja occidentalis*). In *Juniperus Sabina* the acid is associated with sabinic acid (p. 69), from which it is separated by saponifying the waxy portions melting at about 80° C., precipitating the mixture of crude acids and separating the sodium salts by means of four per cent solution of sodium chloride. The insoluble portion consists of the sodium salts of juniperic acid and some other hitherto unidentified acids, whilst the dissolved sodium salts represented almost exclusively the sodium salt of sabinic acid.

The acid melts at 95° C. At the temperature of the melting point inner anhydration seems to take place, as the solidified mass melts at 83° C., and after boiling with alcoholic potash the acid of the melting point 95° is again obtained.

Juniperic acid is insoluble in cold water and only slightly soluble in boiling water (0·2 grm. in 100 c.c.). It dissolves easily in alcohol; is sparingly soluble in acetone (2·5 grms. in 100 c.c.), and dissolves easily in ether and petroleum ether in the hot, but very sparingly only in the cold. All the "salts" including those of the alkali salts are insoluble in water. The alkaline salts are soluble in alcohol and can be recrystallised from it.

Acetyl juniperic acid, $C_{15}H_{30}(O.C_2H_3O)COOH$, melts at 63° C.; it dissolves more easily in ether and benzene than juniperic acid. It is best recrystallised from 60 per cent alcohol.

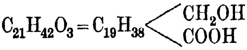
LANOPALMIC ACID, $C_{16}H_{32}O_3$

Lanopalmic acid isolated from that portion of the wool wax acids which forms potash soaps readily soluble in cold alcohol (Vol. II. Chap. XIV. "Wool Wax") crystallises from dilute alcohol in radiated crystals, melting at 87°-88° C., and solidifying at 85°-83° C. It is insoluble in water, but dissolves on boiling in the presence of a small quantity of alcohol, and separates on cooling as a white crystalline magma. The ordinary organic solvents dissolve it readily.

Aqueous alkalis do not readily dissolve the acid; on adding, however, a little alcohol and heating, the alkali salts are formed. They are stated to exist only in hot aqueous solution, and to become dissociated into acid salts, which separate on cooling, and into free alkali.

The *magnesium* salt is insoluble in hot alcohol. The *calcium* salt dissolves easily in boiling absolute alcohol, but sparingly in 95 per cent alcohol.

The existence of this acid would seem to require confirmation.



An acid of the formula $C_{21}H_{42}O_3 = C_{19}H_{38}{<}\begin{smallmatrix}CH_2OH\\COOH\end{smallmatrix}$ is stated to occur, combined with alcohols, in carnaüba wax.[1] The acid does not appear to exist in the free state, since its inner anhydride, or lactone, is obtained whenever the salts of the acid are decomposed with a mineral acid.

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[1] *Compt. rend.*, 1908, 1311; 1910 (150), 875. *Journ. de Pharm. et de Chim.*, 1909 (30), 10.

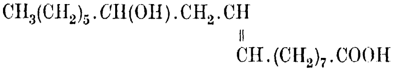
COCCERIC ACID, $C_{31}H_{62}O_3$

Cocceric acid, stated to occur combined with cocceryl alcohol in cochineal wax[2] forms a crystalline powder (from alcohol), melting at 92°-93° C.; it dissolves sparingly in cold alcohol, ether, benzene, petroleum ether, and glacial acetic acid. By oxidation with chromic acid in acetic acid solution a pentadecylic acid is formed.[3]

VII.—ACIDS OF THE RICINOLEIC SERIES. HYDROXYLATED ACIDS $C_nH_{2n-2}O_3$

ACIDS $C_{18}H_{34}O_3$

(a) RICINOLEIC ACID,



$$\begin{array}{l} CH_3(CH_2)_5.CH(OH).CH_2.CH \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \| \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad CH.(CH_2)_7.COOH \end{array}$$

The constitution of the acid is best represented by the formula proposed by *Goldsobel*[4] as given above; it is based on the formation of a ricinostearolic acid, a keto-oxystearic acid which yields two oximes, finally leading to (cp. above, p. 174) dekalactone and azelaïc acid (cp. also *Haller and Brochet*[4]).

Ricinoleic acid (discovered by *Bussy and Lecanu*,[5] and named "ricinoleic acid" by *Saalmüller*,[6] and "acide ricinoléique" by *Swanberg and Kolmodin*[7]) occurs, combined with glycerol, in large quantities in castor oil (see "Castor Oil," Vol. II. Chap. XIV.). The formula $C_{18}H_{34}O_3$ was established by the classical researches of *Bouis*. Crude ricinoleic acid, as obtained by saponifying castor oil and decomposing the soap, represents a thick oil of specific gravity 0·9509 at 15·5° C., solidifying completely on cooling to $-6°$ to $-10°$ C. By gradually pressing the cooled crude acid at temperatures not exceeding 12° C., *Krafft*[8] obtained a white, odourless, hard, crystalline mass melting at 16°-17° C.; this he judged to be pure ricinoleic acid. *Juillard*,[9] however, showed that the acid so prepared still contains stearic and natural dihydroxystearic (see p. 221) acids. The pure acid is best obtained from its barium salt purified by repeated crystallisation from alcohol in which the barium salts of the solid acids are insoluble. According to *Chonowsky*[10] it is preferable to remove the solid fatty acids before the castor oil is saponified. This is done by dissolving castor oil in alcohol and allowing the solution to stand at a low temperature, when a crystalline glyceride, melting at 33° C., separates out.

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[1] *Journ. Soc. Chem. Ind.*, 1884, 448.

[2] *Ibid.*, 1885, 585.

[3] Liebermann and Bellami, *Berichte*, 1887, 962.

[4] Goldsobel, *ibid.*, 1894, 3121; Kasansky, *Journ. f. prakt. Chem.*, 1900 (62), 363; Haller and Brochet, *Compt. rend.*, 1910, 496.

[5] *Journ. Pharm.* 13, 57.

[6] *Liebig's Annal.*, 1848 (64), 108.

[7] *Jahresb.*, 1847, 564.

[8] *Berichte*, 1888, 2734; cp. also Hassenkamp, *Berichte*, 1876, 1916.

[9] *Bull. Soc. Chim.*, 1895 (13), 240.

[10] *Berichte*, 1909, 3340.

Pure ricinoleic acid melts at 4°-5° C.; it is miscible with alcohol and ether in every proportion. It cannot be distilled without undergoing decomposition, even under a pressure of only 15 mm.; among the products of decomposition are found undecylenic acid and œnanthaldehyde,[1] and, according to *Mangold*,[2] in addition thereto, an acid of the formula $C_{18}H_{32}O_2$.[3] Most likely identical with this, is the acid obtained by abstraction of the elements of one molecule of water from ricinoleic acid either in an indirect manner by passing through the di-iodo-derivative or in a direct manner by heating the zinc salt with anhydrous zinc chloride. This unsaturated acid $C_{18}H_{32}O_2$ is isomeric but not identical with linolic acid (*Chonowsky*[4]). On subjecting ricinoleic acid to dry distillation optically active hydrocarbons are obtained.[5]

The ricinoleic acid prepared from castor oil is, like castor oil itself, optically active; this is indicated in the above-given constitutional formula by the presence of one asymmetric carbon atom "*C*" in the molecule. *Walden*[6] found for the liquid acid in a 100 mm. tube $\alpha_D = 6{\cdot}67°$, and for its acetone solution $[\alpha]_D = +6{\cdot}25$ to $+7{\cdot}5°$.

According to *H. Meyer*,[7] ricinoleic acid becomes spontaneously polymerised on standing, with the formation of polyricinoleic acids, which are easily re-converted into ricinoleic acid by boiling with alcoholic potash. Thus, an acid of the specific gravity 0·9460 at 12° C. had become viscous after eight years' standing, its specific gravity having increased to 0·9608 at 12° C.; at the same time the iodine value had decreased from the original number 85·53 to 64·06. *Woldenberg*[8] states that a specimen of ricinoleic acid of the original neutralisation value 188·24 exhibited after five months the neutralisation value 170·9.[9] (Cp. Vol. III. Chap. XV.)

Ricinoleic acid assimilates two atoms of bromine or one molecule of iodochloride, but does not absorb hydrogen on treatment with sodium amalgam. By reducing ricinoleic acid with phosphorus iodide and hydriodic acid, di-iodostearic acid is obtained; the latter yields, on reduction with zinc dust in acetic acid solution, stearic acid (*Chonowsky*[10]). In view of the fact that castor oil can be reduced in the cold,[11] with hydrogen in the presence of colloïdal palladium, to a saturated glyceride, it follows that ricinoleic acid also can be reduced to a saturated acid with hydrogen, either in the cold by using colloïdal palladium as a catalyst, or at higher temperatures by employing nickel as a catalytic substance. If the temperature at which the reduction takes place is kept low, hydroxystearic acid is obtained; at a more elevated temperature the hydroxyl group is split off and stearic acid is formed.[1]

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[1] *Berichte*, 1897, 2034. Cp. also Haller and Brochet, *Compt. rend.*, 1910 (15), 503.

[2] *Ibid.*, 1894, Ref. 629.

[3] *Ibid.*, 1888, 2734; cp. also Hassenkamp, *ibid.*, 1876, 1916.

[4] *Ibid.*, 1909, 3346.

[5] Neuberg and Rosenberg, *Biochem. Zeits.*, 1907, 206. Cp. also Lewkowitsch, *Jahrb. d. Chem.*, 1907 (xvii.), 417.

[6] *Ibid.*, 1894, 3472.

[7] *Arch. d. Pharm.*, 1897 (235), 184.

[8] *Inaug. Dissert.*, Zürich, 1908.

[9] Cp. also Rassow, *Eighth Intern. Cong. App. Chemistry* (see *Chem. Zeit.*, 1912, 1139).

[10] *Berichte*, 1909, 3343.

[11] Paal and Roth, *Berichte*, 1908, 2283.

Nitrous acid transforms ricinoleic acid into its stereoisomeride—*ricinelaïdic* acid.

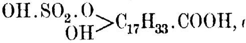
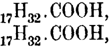
Ricinoleic acid does not absorb oxygen on exposure to the atmosphere. On treatment with ozone, the acid assimilates, according to *Thieme*,[2] four atoms of oxygen, forming a perozonide. With nitrogen tetroxide ricinoleic acid forms an addition product, which is split by fuming hydrochloric acid into heptylic and azelaïc acids (see p. 175, *Jegorow*). With regard to the changes the acid undergoes on blowing with air at elevated temperatures, see Vol. II. Chap. XIV. "Castor Oil."

On oxidising ricinoleic acid with an alkaline solution of potassium permanganate in the cold, two hydroxyl groups are assimilated with formation of trihydroxystearic acid. *Hazura and Grüssner*[3] stated that two isomeric trihydroxystearic acids are formed, and concluded, therefore, that the liquid fatty acid of castor oil is a mixture of two isomerides, viz. *ricinoleic* and *isoricinoleic* acids. The author is, however, of the opinion that this conclusion need not necessarily be adopted, as two stereometrical isomerides may be obtained from one and the same ricinoleic acid.[4] The strictures of the author would seem to be confirmed by *Haller's*[5] statement that he was unable to find two isomeric ricinoleic acids in castor oil (see Vol. II. Chap. XIV. "Castor Oil").

By oxidation with nitric acid suberic and azelaïc acids are obtained.

By treatment of ricinoleic acid with sulphur a plastic mass, claimed as an india-rubber substitute, is obtained.[6]

On boiling ricinoleic acid with acetic anhydride, an anhydride of the acetyl derivative $C_6H_{13}CH(O.C_2H_3O)CH_2.CH=CH(CH_2)_7COOH$ is obtained (cp. Chap. VIII. "Hydroxylated Fatty Acids"). *Kasansky's* statement that acetyl-ricinoleic acid is formed has been refuted by *Grün*.[7] In the latter's opinion the acetylated anhydride of the formula $C_{17}H_{32}(O.C_2H_3O).CO.O.C_{17}H_{32}COOH$ had been formed.

By the action of concentrated sulphuric acid on ricinoleic acid the following products are obtained (*Juillard*[8]):—*ricinoleo-sulphuric acid*, $OH.SO_2.O.C_{17}H_{32}.COOH$, *dihydroxystearo-sulphuric acid*,  $\begin{matrix}OH.SO_2.O\\OH\end{matrix}\!\!>C_{17}H_{33}.COOH$, *dibasic diricinoleic acid*,  $O<\begin{matrix}C_{17}H_{32}.COOH,\\C_{17}H_{32}.COOH,\end{matrix}$ *monobasic diricinoleic acid*, $OH.C_{17}H_{32}.COO.C_{17}H_{32}.COOH$, *dihydroxy-*

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[1] Cp. Engl. pat. 13,519, 1911; French pat. 433,294, K. E. Markel and J. Crosfield and Sons, Ltd. Fokin, *Journ. Russ. Phys. Chem. Soc.*, 1912 (44), 653, states that by the catalytic reduction of ricinoleic acid with platinous hydroxide he obtained λ-hydroxystearic acid. It may also be pointed out that Woldenberg (*Inaug. Dissert.*, Zürich, 1908) could not reduce ricinoleic acid by a current of hydrogen with platinum as a catalyst, whereas under the same conditions the methylester of ricinoleic acid was readily reduced to the methylester of 1, 12 hydroxystearic acid.

[2] *Inaug. Dissert.*, Kiel, 1906.

[3] *Monatsh. f. Chem.*, 1888 (9), 469.

[4] Cp. Mangold, *Berichte*, 1894, Ref. 629.

[5] *Compt. rend.*, 1907 (144), 462.

[6] Chem. Werke, vorm. Dr. H. Byk, German patent 252,193.

[7] *Berichte*, 1909, 3761. Cp. Rassow, *Zeits. f. angew. Chem.*, 1913, 318.

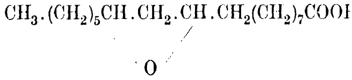
[8] *Bull. Soc. Chim.*, 1894 (11), 280. The isoricinoleic acid described by Juillard appears to be a ketonic acid, and is a by-product formed by the action of sulphuric acid on ricinoleic acid; it is differentiated from ricinoleic acid by its solubility in petroleum ether.

stearic acid, $C_{18}H_{36}O_4$, melting at 66°-68° C., *a solid acid*, $C_{36}H_{70}O_7$, and *isoricinoleic acid*, $C_{18}H_{34}O_3$ (cp. Vol. III. Chap. XV. " Turkey-red Oils ").

Grün [1] showed that the *dihydroxystearic acid* melting at 66°-68° C. consisted of a mixture of several isomerides; for by fractional crystallisation of this dihydroxystearic acid he obtained two optically inactive isomerides melting at 69·5° and 108° C. respectively; an optically active acid melting at 90° C., and a small amount of another inactive acid melting at 126° C. The acids melting at 69·5° C. and 90° C. respectively have the constitution of a 9, 12-dihydroxystearic acid; hence the inactive acid of the melting point 69·5° C. is judged to be a racemic compound. The optically active acid melting at 90° C. is converted into the racemic compound melting at 69·5° C. on keeping for some time in alcoholic solution, or more rapidly by heating the solution to 130°-140° C. If acetyl ricinoleic acid be treated with an equal amount of concentrated sulphuric acid, ricinoleo-sulphuric acid is obtained, the acetyl group being replaced by the SO_3H group. If, however, sulphuric acid be allowed to act upon the chloro-oleic acid, $CH_3(CH_2)_5CHCl.CH_2.CH=CH(CH_2)_7COOH$, evolution of hydrochloric acid takes place even below the temperature of the freezing point.[2]

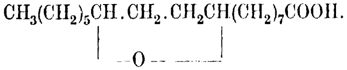
Woldenberg [3] studied the gradual change taking place when equimolecular amounts of ricinoleic and concentrated sulphuric acids are mixed, and found that the iodine value of the mixture gradually decreased within 115 hours from the theoretical value 64·04 to 48·4, the neutralisation value from the theoretical value 425 to 279·79; the amount of free ricinoleic acid decreased very rapidly (from the original 75·38 per cent in the mixture) to 5·93 per cent, and had fallen to zero after (about) 40 hours.

Chonowsky,[4] who carried out the same experiment, arrives at the conclusion that two isomeric *glycid acids* are formed having the following formulæ respectively,



$$\mathrm{CH_3.(CH_2)_5\underbrace{CH.CH_2.CH}_{O}.CH_2(CH_2)_7COOH}$$

and



$$\mathrm{CH_3(CH_2)_5\underbrace{CH.CH_2.CH_2CH}_{O}(CH_2)_7COOH.}$$

With these two acids small quantities of a dihydroxylated acid are admixed which is considered to be identical with the dihydroxystearic acid melting at 116°-117° C. and obtained from di-iodo-stearic acid (see p. 229). The first of these two glycids yields on digestion with acetic anhydride a diacetyl-derivative. *Grün* [5] raises objections to these conclusions and explains *Chonowsky's* results by pointing out that the latter overlooked the formation of intermediate products.

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[1] *Berichte*, 1906, 4400; 1909, 3759. Wetterkamp, *Inaug. Dissert.*, Zürich, 1909, *Zeits. f. Farbenindustrie*, 1909, No. 18.

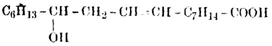
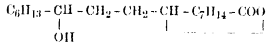
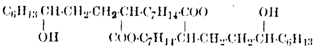
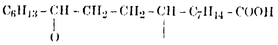
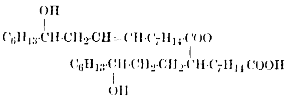
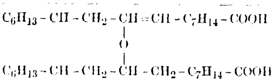
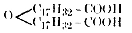
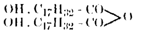
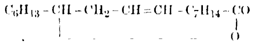
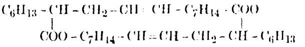
[2] Cp. Grün and Wetterkamp, *Zeits. f. Farbenind.*, 1908, 375. Woldenberg, *Inaug. Dissert.*, Zürich, 1908.

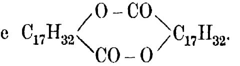
[3] *Inaug. Dissert.*, Zürich, 1909.

[4] *Berichte*, 1909, 3339.

[5] *Ibid.*, 1909, 3761.

The following table reproduces a number of characteristics of ricinoleic acid and the most important products that can be obtained from it by the action of sulphuric acid, as compiled by *J. Rubinsky.*[1]

		Molecular Weight.	Neutralisation Value.	Saponification Value.	Acetyl Value.	Iodine Value.
Ricinoleic acid	 $C_6H_{13}-\underset{\substack{\mid\\OH}}{CH}-CH_2-CH=CH-C_7H_{14}-COOH$	298·3	188·1	188·1	188·1	85·2
Saturated lactone . .	 $C_6H_{13}-\underset{\substack{\mid\\OH}}{CH}-CH_2-CH_2-\underset{\mid}{CH}-C_7H_{14}-\underset{\mid}{COO}$	298·3	0	188·1	188·1	0
Saturated lactide . . .	 $\begin{array}{l}C_6H_{13}\underset{\substack{\mid\\OH}}{CH}\cdot CH_2\cdot CH_2\cdot\underset{\mid}{CH}\cdot C_7H_{14}\cdot\underset{\mid}{COO}\\ \qquad COO\cdot C_7H_{14}\cdot CH\cdot CH_2\cdot CH_2\cdot\overset{\substack{OH\\\mid}}{CH}\cdot C_6H_{13}\end{array}$	596·5	0	188·1	188·1	0
Glycid acid .	 $C_6H_{13}-\underset{\substack{\mid\\O}}{CH}-CH_2-CH_2-\underset{\mid}{CH}-C_7H_{14}-COOH$	298·3	188·1	188·1	0	0
Semisaturated diricinoleic acid . . .	 $\begin{array}{l}C_6H_{13}\cdot\overset{\substack{OH\\\mid}}{CH}\cdot CH_2\cdot CH=CH\cdot C_7H_{14}\cdot\underset{\mid}{COO}\\ \qquad C_6H_{13}\cdot\underset{\substack{\mid\\OH}}{CH}\cdot CH_2\cdot CH_2\cdot CH\cdot C_7H_{14}COOH\end{array}$	596·5	94·1	188·1	188·1	42·6
Semisaturated dibasic diricinoleic acid	 $\begin{array}{l}C_6H_{13}-CH-CH_2-\underset{\substack{\mid\\O\\\mid}}{CH}=CH-C_7H_{14}-COOH\\ C_6H_{13}-CH-CH_2-CH-CH_2-C_7H_{14}-COOH\end{array}$	596·5	188·1	188·1	94·1	42·6
Dibasic diricinoleic acid	 $O<\begin{array}{l}C_{17}H_{32}-COOH\\C_{17}H_{32}-COOH\end{array}$	578·5	194·2	194·2	0	87·8
Ricinoleic anhydride . .	 $\begin{array}{l}OH.C_{17}H_{32}-CO\\OH.C_{17}H_{32}-CO\end{array}>O$	578·5	0	194·2	194·2	87·8
Unsaturated lactone . .	 $C_6H_{13}-\underset{\mid}{CH}-CH_2-CH=CH-C_7H_{14}-\underset{\substack{\mid\\O}}{CO}$	280·2	0	200·4	0	90·6
Unsaturated lactide . .	 $\begin{array}{l}C_6H_{13}-\underset{\mid}{CH}-CH_2-CH=CH-C_7H_{14}-\underset{\mid}{COO}\\ \quad COO-C_7H_{14}-CH=CH-CH_2-CH-C_6H_{13}\end{array}$	560·5	0	200·4	0	90·6
Polyricinoleic acids :—						
(*a*) Diricinoleic acid	$OH.C_{17}H_{32}-COO.C_{17}H_{32}-COOH$	578·5	97·1	194·2	97·1	87·8
(*b*) Triricinoleic acid	$OH(C_{17}H_{32}.COO)_2C_{17}H_{32}-COOH$	858·7	65·4	196·2	65·4	88·8
(*c*) Tetraricinoleic acid	$OH(C_{17}H_{32}.COO)_3C_{17}H_{32}-COOH$	1139·0	49·3	197·2	49·3	89·2
(*d*) Pentaricinoleic acid	$OH(C_{17}H_{32}.COO)_4C_{17}H_{32}-COOH$	1419·2	39·8	197·9	39·6	89·5
(*e*) Hexaricinoleic acid	$OH(C_{17}H_{32}.COO)_5C_{17}H_{32}-COOH$	1699·5	33·0	198·0	33·0	89·7

Ricinoleo-sulphuric acid, $C_{17}H_{32}(O.SO_3H)COOH$, is prepared in its pure state by allowing chlorosulphonic acid to act on ricinoleic acid in a solution of absolute ether (*Woldenberg*[1]). Its formation by the action of concentrated sulphuric acid on ricinoleic acid has been described above. The acid is soluble in ten parts of water and forms a clear solution. By prolonged standing of ricinoleo-sulphuric acid with water (cp. also Vol. III. Chap. XV.), the acid is hydrolysed, sulphuric acid being split off. The hydrolysis becomes accelerated by heating the solution to boiling or by adding dilute mineral acids. The total amount of acid is, however, not resolved into sulphuric acid and ricinoleic acid, but the ricinoleic ester of ricinoleic acid, $C_{17}H_{32}(OH)COO.C_{17}H_{32}COOH$, is formed, which is converted partially by the loss of one molecule of water into the lactide  The formation of the lactide is arrested when the proportion of the lactide to the ricinoleic ester of ricinoleic acid equals 2 : 1.[2]

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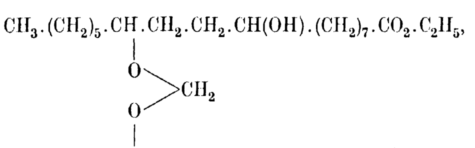
[1] *Inaug. Dissert.*, Borna-Leipzig, 1912. Cp. *Zeits. f. angew. Chem.*, 1913, 316.

Ricinoleic acid yields on treatment with gaseous hydrobromic acid in the cold, according to the conditions of the experiment, monobromo- or dibromo-stearic acid (*Kasansky*[3]). On reducing these compounds the ordinary stearic acid was obtained; hence it is evident that the hydroxyl group in ricinoleic acid had been replaced by bromine. If the substitution of the hydroxyl group be prevented by previous acetylation of the OH group, an acetylated hydroxystearic acid is ultimately obtained. The hydroxystearic acid resulting from this acetylated hydroxy acid differs from the hitherto known isomerides. By the action of hydriodic acid on ricinoleic acid the hydroxyl group is replaced by an atom of iodine; at the same time a second atom of iodine is assimilated, so that a di-iodo-stearic acid results (*Chonowsky*[4]).

Dry hydrogen chloride is not assimilated by ricinoleic acid. In the presence of *formaldehyde* dry hydrogen chloride produces in an alcoholic solution of ricinoleic acid condensation to *ethyl methylene-dioxydistearate*, to which *Tschilikin*[5] ascribes the formula :—



Endeavours to isolate the free acid led to the formation of condensation products. This is a saturated substance. (It will be observed that *Tschilikin* places the OH group in a different position from that indicated above.)

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[1] *Inaug. Dissert.*, Zürich, 1908.

[2] Grün and Wetterkamp, *Zeits. f. Farbenindustrie*, 1909, Heft 18. Wetterkamp, *Inaug. Dissert.*, Zürich, 1909.

[3] *Journ f. prakt. Chem.*, 1900 (62), 363.

[4] *Berichte*, 1909, 3342.

[5] *Journ. Russ. Phys. Chem. Soc.*, 1912 (44), 515 ; cp. also *Revue génér. des matières colorantes*, 1911 (15), 33.

Dibromoricinoleic acid, $CH_3.(CH_2)_5.CH(OH)CH_2.CHBr.CHBr.(CH_2)_7.COOH$, forms a thick, slightly yellowish oil (*Ulrich*,[1] *Woldenberg*[2]). The sulphuric ester is obtained by allowing chlorosulphonic acid to act on the dibromide in ethereal solution. By boiling with concentrated alcoholic potash, ricinostearolic acid is obtained.

Ricinoleic acid, as prepared from castor oil by saponification and subsequent acidification of the soap is a commercial product, used in the textile industry (see Vol. III. Chap. XV. " Sulphonated Oils "). An *acid ammonium salt* of the acid prepared by neutralising crude ricinoleic acid with ammonia and adding a second equivalent of ricinoleic acid is also obtainable in commerce.

Sodium ricinoleate[3] is a soft doubly-refracting substance, solidifying on cooling to a waxy mass.

Most of the metallic salts of ricinoleic acid are readily obtained in the crystalline state; they behave with solvents very much like the corresponding salts of oleic acid. *Calcium*, as also *barium ricinoleate*, are soluble in warm alcohol; the *barium* salt, even when repeatedly recrystallised from alcohol, retains water, which is not even given off at 120° C. The *barium* salt is practically insoluble in ether (*Woldenberg*, *Chonowsky*) and petroleum ether (*Woldenberg*). *Lead ricinoleate* melts at 100° C. and is easily soluble in ether, but practically insoluble in low-boiling petroleum ether.[4]

Methylester.—*Rochleder* first prepared this ester by passing hydrochloric acid gas through a solution of castor oil in alcohol (cp. " Alcoholysis," p. 100). Specific gravity 0·9236, boiling point 245° C. under a pressure of 10 mm. $[\alpha]_D = +3{\cdot}8^\circ$ (*Walden*). The progress of the action of concentrated sulphuric acid on this ester has been studied by *Woldenberg*.[5]

Ozone converts the methylester into the perozonide ($C_{19}H_{36}O_7$) which is resolved by treatment with sodium carbonate and sodium bisulphite into optically active β-hydroxypelargonic acid ($CH_3.(CH_2)_5 CH(OH).COOH$), azelaic acid, methylester of azelaic acid and the corresponding semi-aldehydes (*Haller and Brochet*[6]). The reduction of the methylester to a saturated substance has been referred to, p. 215, footnote 1.

Ethylester.—Specific gravity 0·9145, boiling point 258° C. under a pressure of 13 mm. $[\alpha]_D = +4{\cdot}07^\circ$ (*Walden*).

Haller[7] ascertained the following constants of ricinoleic esters :—

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[1] *Zeits. f. Chem.*, 1867 (3), 545.

[2] *Inaug. Dissert.*, Zürich, 1908.

[3] Vorlaender, *Berichte*, 1910, 3125.

[4] Lane, *Journ. Soc. Chem. Ind.*, 1907, 597.

[5] *Inaug. Dissert.*, Zürich, 1908.

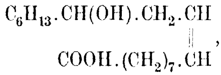
[6] *Compt. rend.*, 1910 (150), 503 ; *Chem. Zeit.*, 1910, 289.

[7] *Compt. rend.*, 1907 (144), 462.

[Table

Esters of Ricinoleic Acid.	Boiling Point under 10 mm. Pressure. °C.	Specific Gravity at 15° C.	Specific Rotation. $[\alpha]_D$.	Refractive Index. n^{15}_D.
Methyl . . .	225-227	0·927	+5°2′	1·4645
Ethyl . . .	227-230	0·918	+4·48°	1·4630
Propyl (normal) .	233-236	0·912	+4·35°	1·4624
Isobutyl . .	239-241	0·908	+4·22°	1·4621

On oxidising the methylester of ricinoleic acid with potassium permanganate in acetone solution, *Haller* obtained only one trihydroxystearic ester, melting at 87° C. By subjecting the methylester to dry distillation, 62 per cent of the theoretical œnanthic aldehyde and 40 per cent of undecylenic methylester were obtained. In the case of the ethylester the corresponding figures were 50 per cent and 32 per cent respectively.

Ricinelaïdic acid,  $\begin{array}{c} C_6H_{13}.CH(OH).CH_2.CH \\ \| \\ COOH.(CH_2)_7.CH \end{array}$, the stereometric isomeride of ricinoleic acid, is obtained from the latter by the action of nitrous acid. *Wetterkamp* obtained a better yield by adding nitric acid, specific gravity 1·2, in small proportions to ricinoleic acid previously cooled to −5° C. and keeping the temperature at −5° C. to 0°. The acid is optically active. $[\alpha]_D = +6{\cdot}67°$ (c = 12) in a solution of absolute alcohol. Ricinelaïdic acid crystallises in needles melting at 52°-53° C., 53°-54° C. (*Woldenberg*). As regards absorption of bromine, iodochloride, and oxygen, it behaves like ricinoleic acid. On oxidising ricinelaïdic acid with potassium permanganate in alkaline solution, two isomeric (most likely stereometric) trihydroxylated acids are formed (*Mangold*). On distilling ricinelaïdic acid *in vacuo*, *Mangold*[1] obtained an unsaturated acid, $C_{18}H_{32}O_2$, crystallising from alcohol in shining plates melting at 53°-54° C. It is doubtful whether this acid is identical with the acid $C_{18}H_{32}O_2$ obtained in the same manner from ricinoleic acid.

Ricinelaïdo-sulphuric acid, $C_{17}H_{32}.(O.SO_3H)COOH$, is obtained by the action of chlorosulphonic acid on ricinelaïdic acid. The aqueous solution of the acid undergoes on heating the same changes which have been detailed in the case of the sulphuric ester of ricinoleic acid (see above).

Ricinic acid was obtained by *Krafft*[2] on heating barium ricinoleate in a vacuum, when the barium salt of ricinic acid remains in the retort. On decomposing this salt with a mineral acid, ricinic acid is liberated. The acid can be purified by fractionating *in vacuo*; it then forms glistening laminæ (from alcohol), melting at 81° C.; it boils under 15 mm. pressure with very slight decomposition.

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[1] *Monatsh. f. Chem.*, 1894 (15), 309.

[2] Cp. also Walden, *Berichte*, 1894, 3472.

(b) QUINCE OIL ACID

A hydroxylated acid, $C_{17}H_{32}(OH)COOH$, is stated by *Herrmann*[1] to occur in quince oil. It differs from ricinoleic and its isomeric acids, in that its dibromide melts at 108° C., whereas ricinoleic and ricinelaïdic dibromides are liquid (cp. Chapter VIII.).

VIII.—ACIDS OF THE SERIES $C_nH_{2n}O_4$. DIHYDROXYLATED ACIDS

DIHYDROXYSTEARIC ACID, $C_{18}H_{36}O_4$

The natural dihydroxylated acid, occurring in castor oil to the extent of about 1 per cent (*Juillard*[2]), is obtained by cooling the mixed fatty acids of castor oil below 12° C., and keeping them thereat for some time. The crystalline magma is allowed to drain, and is then pressed and recrystallised from alcohol, whereby a mixture of dihydroxystearic and stearic acids is obtained. The latter is removed by washing with hot toluene, and the remaining crude dihydroxystearic acid is recrystallised from boiling alcohol.

H. Meyer[3] prepares the acid by decomposing the lime salts of the mixed castor oil acids with hydrochloric acid, and allowing to crystallise from ether in the cold. After twelve hours' standing crystals melting at 140° to 141° C. are obtained.

The pure acid melts at 141° to 143° C.; it is insoluble in ether, petroleum ether, and benzene, slightly soluble in cold toluene, more so in the hot solvent; it dissolves in boiling alcohol and boiling acetic acid. Reducing agents readily convert the acid into stearic acid. By treatment with hydrochloric acid at 180° C., and subsequently with caustic potash, it is converted into the dibasic acid:—$COOH.(OH)C_{17}H_{33}.O.C_{17}H_{33}(OH)COOH$.

Probably this acid—being a natural product—is optically active.

The *sodium salt* forms fine needles.
Methylester, melts at 106°-108° C.
Ethylester, melts at 104°-106° C.

LANOCERIC ACID, $C_{30}H_{60}O_4$

This acid was isolated from the mixture of soaps obtained on saponifying wool wax with alcoholic potash.[4]

The acid crystallises from alcohol in microscopic laminæ; it softens at 102° C. and melts at 104°-105° C.; it then solidifies at 103°-101° C., to melt again at 102° C. It thereby loses one molecule of water, probably from the two hydroxyl groups, for it still possesses acid properties. Lanoceric acid readily forms a lactone, *e.g.* when boiled with dilute hydrochloric acid; the lactone melts at 86° C. This lactone is probably identical with "lanocerin" recently found in wool wax by *Röhmann*[1] (cp. also Vol. II. Chap. XIV. "Wool Wax").

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[1] *Arch. d. Pharm.*, 1899 (237), 366.

[2] *Bull. Soc. Chim.*, 1895 (13), 238. The dihydroxystearic acid which Benedikt and Ulzer (*Monatsh. f. Chem.*, 1887 (8), 208) isolated from a "Turkey-red oil" is not, as they stated, an artificial product, but nothing else than this natural hydroxystearic acid (Grün, *Berichte*, 1906, 4400); cp., however, p. 216.

[3] *Arch. d. Pharm.*, 1897, 184; *Chem. Revue*, 1897, 223.

[4] Darmstaedter and Lifschütz, *Berichte*, 1896, 1474, 2893; *Journ. Soc. Chem. Ind.*, 1896, 543. (The acid is described there as lanocerinic acid.)

Lanoceric acid is almost insoluble in cold water and in alcohol, but is readily soluble in hot alcohol. It does not combine easily with aqueous potash; a little alcohol, however, readily induces combination. The salt is therefore best prepared in alcoholic solution. The *potassium* salt behaves like that of lanopalmic acid (p. 212), in that it dissociates on cooling into the acid salt, which separates, and into free alkali.

IX.—ACIDS OF THE SERIES $C_nH_{2n-2}O_4$, DIBASIC ACIDS

The dibasic acids belonging to this series have been isolated from Japan wax (see Vol. II. Chap. XIV. "Japan Wax") by fractionating its insoluble mixed fatty acids *in vacuo*. The composition of the acids was established from that of the hydrocarbons which they yield on dry distillation with barium oxide under reduced pressure.

HEPTADECAMETHYLENE-DICARBOXYLIC ACID,[2] $C_{17}H_{34}(COOH)_2$

This acid yields normal heptadecane.

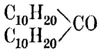
OCTODECAMETHYLENE-DICARBOXYLIC ACID,[2] $C_{18}H_{36}(COOH)_2$

This acid yields normal octodecane.

JAPANIC ACID (NONADECAMETHYLENE-DICARBOXYLIC ACID), $C_{21}H_{40}O_4 = C_{19}H_{38}(COOH)_2$

Japanic acid[3] is the first dibasic acid identified in natural fats. Most likely it forms a mixed glyceride together with palmitic acid (see Vol. II. Chap. XIV. "Japan Wax").

The acid crystallises from alcohol and chloroform in white laminæ melting at 117·7°-117·9° C. The crystals dissolve very sparingly in most solvents. Japanic acid is heavier than water.

On heating the acid to 200° C., carbon dioxide is given off with the formation of the ketone  $\begin{matrix}C_{10}H_{20}\\C_{10}H_{20}\end{matrix}\!\!>CO$ melting at 82°-83° C. On distilling with barium hydroxide *in vacuo* normal nonadecane is obtained.[3]

The *potassium* salt is sparingly soluble in 95 per cent alcohol, 100 c.c. of which dissolve 0·1345 grm. at 26° C.

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[1] *Centralbl. f. Physiol.*, 1905, xix. No. 10.

[2] R. Schaal, *Berichte*, 1907, 4784.

[3] L. A. Eberhardt, *Inaug. Dissert.*, Strassburg, 1888; Geitel and v. d. Want, *Journ. f. prakt. Chem.*, 1900 (61), 151.

On heating the *silver* salt with ethyliodide, the *ethylester*, melting at 53° C., is obtained.

OXIDATION PRODUCTS OF FATTY ACIDS

The above-described acids (with the exception of the isomerides mentioned under the headings of the naturally occurring acids) are met with in natural fats and waxes. Besides these, there are found in various products of the fat industries several saturated hydroxylated acids, as also their inner anhydrides. These are described below, together with some other hydroxylated fatty acids, which are of great importance for the identification of glycerides of unsaturated acids.

Other derivatives of the fatty acids obtained indirectly by oxidation are *ketones*, a list of which has been given above. These ketones appear to be of importance from a physiological point of view, as representing the intermediate stages of degradation of the higher fatty acids in the animal organism. Too little is known at present to justify more than a passing reference here (cp. also above, p. 55).

Greater importance attaches to the unsaturated fatty acids of the *stearolic group*, which are also obtained by a process of indirect oxidation. They represent intermediate products standing between unsaturated fatty acids and the cleavage products into which they are ultimately broken down. Thus they are of importance in determining the constitution of unsaturated acids, as has been pointed out above on p. 174. The acids belonging to the stearolic series are *isomeric* with the acids of the linolic series.

Just as the acids of the oleic series lead to the acids of the stearolic series, so do the acids of the ricinolic series lead to acids which may be termed acids of the *ricinostearolic* series.

In the course of oxidation of fatty acids by means of potassium permanganate, or nitric acid, further in the decomposition of the ozone and nitrogen tetroxide addition products of unsaturated fatty acids, a number of *dibasic* acids are formed, the composition of which lends valuable help in the identification of the products of cleavage, and thus in the determination of the constitution of the fatty acids from which they have been derived.

Derivatives of the fatty acids mentioned in the foregoing lines will be described under the following headings :—

I. Hydroxylated acids, $C_nH_m(OH)_xO_2$ ($x = 2n - m$).
II. Acids of the stearolic series, $C_nH_{2n-4}O_2$.
III. Acids of the ricinostearolic series, $C_nH_{2n-4}O_3$.
IV. Dibasic acids, $C_nH_{2n-2}O_4$.

I.—HYDROXYLATED ACIDS, $C_nH_m(OH)_xO_2$

Most of these hydroxylated acids are obtained by oxidising unsaturated acids with dilute potassium permanganate in alkaline solution. The details of this method will be fully described in Chapter VIII.

Saytzeff,[1] as also *Hazura* [2] (who collaborated with *Bauer*, *Friedreich*, and *Grüssner*), derived from their researches the following rule: All unsaturated fatty acids assimilate on oxidation with potassium permanganate in alkaline solution in the cold, as many hydroxyl groups as there are unsaturated carbon atoms in the molecule, yielding saturated hydroxylated acids which contain the same number of carbon atoms in the molecule. Further experiments must decide whether this rule holds good for all unsaturated acids (cp. "Jecoric Acid," p. 209). This reaction, however, is not a quantitative one, as is the case in the formation of the bromo- and iodochloro-derivatives, for, owing to further oxidation, perhaps, of the hydroxylated acids, dibasic acids are also formed.

Hydroxylated acids are also obtained by digesting bromo-derivatives of unsaturated fatty acids with silver hydroxide.

In the following table the hydroxylated acids obtained hitherto by oxidation with potassium permanganate and by means of silver hydroxide are enumerated :—

Fatty Acids.	Hydroxylated Acid.
Tiglic	(Dihydroxytiglic) tigliceric.
Hypogæic	Dihydroxypalmitic.
Palmitoleic	Dihydroxypalmitoleic.
Chaulmoogric	α-Dihydroxydihydrochaulmoogric. β-Dihydroxydihydrochaulmoogric.
Oleic	Dihydroxystearic.
Elaïdic	Dihydroxystearidic.
"Isoöleic"	"Para-dihydroxystearic."
Petroselinic	Dihydroxy petroselinic.
Liver oleic	Dihydroxy acid.
(Unknown)	Dihydroxyjecoleic (?).
Ricinoleic	Trihydroxystearic. α-Isotrihydroxystearic (? see p. 215).
Ricinelaïdic	β-Isotrihydroxystearic (? see p. 220). γ-Isotrihydroxystearic.
Linolic	Tetrahydroxystearic (sativic).
Linolenic	Hexahydroxystearic (linusic).
Isolinolenic (?)	Isolinusic.
Gadoleic	Dihydroxygadoleic.
Erucic	Dihydroxybehenic.
Brassidic	Isodihydroxybehenic.
Isoerucic	Para-dihydroxybehenic.
Arachidonic	Octohydroxystearic.

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[1] *Journ. f. prakt. Chemie*, 1886 (33), 300; 1889 (39), 346.

[2] *Journ. Soc. Chem. Ind.*, 1888, 506.

HYDROXYLATED ACIDS

1. Monohydroxylated Acids, $C_{18}H_{36}O_3 = C_{17}H_{34}(OH)(COOH)$

(*a*) ι (or 1, 10) HYDROXYSTEARIC ACID, $C_{18}H_{36}O_3 = C_{18}H_{35}O_2(OH) = CH_3.(CH_2)_7.CH.(OH).(CH_2)_8COOH$ [1]

This acid is obtained together with stearic acid hydrogen sulphate and stearolactone [2] on dissolving ordinary oleic acid or elaïdic acid in concentrated sulphuric acid (cp. also Vol. III. Chap. XV. "Turkey-red Oils"). The glyceride of this hydroxystearic acid is obtained on subjecting triolein to the same treatment.

This acid is prepared commercially by treating a solution of oleic acid in petroleum ether with concentrated sulphuric acid. Only part of the oleic acid is transformed into hydroxystearic acid; in order to obtain a higher yield of the latter, the unchanged oleic acid must be treated again in the same manner, but even then the yield is not a quantitative one (cp. United States patent 772,129, and Vol. III. Chap. XV. "Conversion of Oleic Acid into Candle Material").

ι-Hydroxystearic acid crystallises (from alcohol) in hexagonal plates, melting at 81°-81·5° C. (*Geitel*), 83°-85° C. (*Saytzeff*), and solidifying at 68°-65° C. 100 parts of absolute alcohol dissolve 8·78 parts at 20° C.; 100 parts of ether at the same temperature dissolve 2·3 parts.

On heating the acid to 200° C., with or without zinc chloride, a viscous mass is obtained, which contains the anhydride $C_{18}H_{34}O_2$, as also oleic acid.[3] By boiling the anhydride with caustic potash hydroxystearic acid is regenerated. On distilling ι-hydroxystearic acid in a vacuum, a portion of the acid passes over unchanged, whilst another portion is converted into oleic and "iso-oleic" acids. By carefully oxidising ι-hydroxystearic acid with chromic acid in acetic acid solution, 10-ketostearic acid, $CH_3(CH_2)_7.CO.(CH_2)_8COOH$, is obtained, whilst sebacic, azelaïc, and very small quantities of suberic acid are formed as by-products (*Shukoff and Schestakoff* [4]).

The *sodium*, *zinc*, and *copper* salts are soluble in alcohol; the *barium* salt is insoluble in both alcohol and ether.

(*b*) κ (or 1, 11)-HYDROXYSTEARIC ACID, $CH_3.(CH_2)_6.CH(OH).CH_2.(CH_2)_8.COOH$ [4]

This acid is obtained, together with the isomeric ι-hydroxystearic acid, on treating "iso-oleic" acid with sulphuric acid in the manner described for ordinary oleic acid. The lower the temperature, the larger is the yield of κ-hydroxystearic acid. κ-Hydroxystearic acid is also formed on digesting the iodo-stearic acid obtained from " iso-oleic " acid and hydriodic acid, with silver hydroxide.

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[1] Shukoff and Schestakoff, *Journ. f. prakt. Chem.*, 1903 (67), 415. Formerly (see p. 121 of the third edition of this work) this acid was described as β-hydroxystearic acid. The true β-hydroxystearic acid, $C_{15}H_{31}.CH(OH).CH_2.COOH$, prepared by Ponzio (*Gazz. chim.*, 1905 (35), ii. 132) melts at 89° C.

[2] Cp. also David, *Compt. rend.*, 1897 (124), 466.

[3] It may be pointed out here that the anhydride, $C_{18}H_{34}O_2$ being a saturated compound, does not absorb iodine; therefore the oleic acid can be determined quantitatively in the mixture (cp. Chap. VI.). According to Shukoff and Schestakoff, this anhydride is γ-stearolactone.

[4] Shukoff and Schestakoff, *Journ. f. prakt. Chem.*, 1903 (67) 417. Formerly (see p. 122 of the third edition of this work) this acid was described as α-hydroxystearic

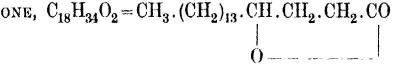
κ-Hydroxystearic acid distils unchanged under a pressure of 100 mm. (difference from ι-hydroxystearic acid), and crystallises (from alcohol) in plates melting at 77°-79° C. *Shukoff and Schestakoff* find 84° C. It is more easily soluble in ether than its ι-isomeride, whilst less readily soluble in absolute alcohol, 100 parts of which dissolve at 20° C. only 0·58 parts of the acid.

On oxidising κ-hydroxystearic acid with chromic acid in acetic acid solution, *Shukoff and Schestakoff* obtained sebacic acid, a dicarboxylic acid, $C_{11}H_{20}O_4$, melting at 124° C. and 11-ketostearic acid, which differs from the 10-ketostearic acid prepared from ι-hydroxystearic acid by the same method.

On treatment with concentrated sulphuric acid γ-stearolactone[1] is obtained.

(γ-HYDROXYSTEARIC ACID, $CH_3.(CH_2)_{13}.CH(OH).CH_2.CH_2.COOH$)

STEAROLACTONE,



$$C_{18}H_{34}O_2 = CH_3.(CH_2)_{13}.\underbrace{CH.CH_2.CH_2.CO}_{O}$$

The free acid has not been prepared yet, for whenever the free acid may be expected its inner anhydride, or lactone, is formed. The lactone is obtained together with ι-hydroxystearic acid when concentrated sulphuric acid is allowed to act on ordinary oleic acid.[2] It is also obtained by heating oleic acid with 10 per cent of zinc chloride to 185° C. (see Vol. III. Chap. XV. " Conversion of Oleic Acid into Candle Material ").

According to *Shukoff and Schestakoff*,[1] stearolactone as obtained (in a yield of 35 per cent) by the action of concentrated sulphuric acid on commercial oleic acid has the iodine number 16-20, and, assuming it to be a monobasic acid, the mean molecular weight 375, which, after boiling with alcoholic potassium hydroxide, falls to 291. This points to the presence of an anhydride similar or analogous to those formed on heating hydroxystearic acid. After distillation the iodine value increases considerably.

If pure stearolactone is treated with sulphuric acid it is partly converted into soluble, acid products, which are probably sulphonic acids.

Stearolactone forms fine white crystalline laminæ melting at 47°-48° C.; it can be distilled almost unchanged. It is insoluble in water, and dissolves easily in alcohol, ether, and petroleum ether. Boiling

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acid. The true α-hydroxystearic acid, $C_{15}H_{31}.CH_2.CH(OH)COOH$, was prepared by Hell and Sadomsky (*Berichte*, 1891, 2391), Le Sueur (*Journ. Chem. Soc.*, 1904, 1709), and Ponzio (*Gazz. chim. ital.*, 1904 (34), 77); it melts at 91°-92° C.

[1] *Journ. Russ. Phys.-Chem. Soc.*, 1908 (40), 830.

[2] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1897, 392.

solutions of alkalis dissolve the stearolactone with the formation of salts of γ-hydroxystearic acid. On adding a mineral acid to such solutions, stearolactone, but not the free acid, is obtained. Provided the above-given constitutional formula be correct, an assumption which stands in need of experimental corroboration, a migration of the double bond must have taken place.

(c) λ (or 1, 12) Hydroxystearic Acid, $CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOH$

This acid is best prepared from its methylester. It melts at 78° C.; it is soluble in alcohol, ether, and chloroform, but is insoluble in petroleum ether and water (*Woldenberg*[1]).

Methylester, $CH_3(CH_2)_5CH(OH)(CH_2)_{10}COOCH_3$, is obtained from the methylester of ricinoleic acid by reduction with hydrogen in the presence of platinum as a catalyst.

With regard to derivatives of *Hydroxybehenic Acid* cp. *D. Warmbrunn.*[2]

2. Dihydroxylated Acids

●(Dihydroxytiglic) Tigliceric Acid,[3] $C_5H_{10}O_4 = C_5H_8O_2(OH)_2$

Tigliceric acid is obtained by oxidising tiglic acid with potassium permanganate. The acid crystallises (from ether) in small plates, melting at 88° C. It is readily soluble in water, alcohol, and acetone, but insoluble in petroleum ether, chloroform, and benzene.

Dihydroxylated Acids, $C_{16}H_{30}O_2(OH)_2$

(a) Dihydroxypalmitic Acid, $C_{16}H_{30}O_2(OH)_2$

This acid, obtained synthetically from dibromopalmitic acid (dibromo-addition product of hypogæic acid) by boiling with silver hydroxide, forms small laminæ (from alcohol) melting at 115° C., and readily soluble in alcohol and in ether.

(b) Dihydroxypalmitoleic Acid, $C_{16}H_{30}O_2(OH)_2$

This acid[4] obtained by *Bull* by oxidising palmitoleic acid, $C_{16}H_{30}O_2$, obtained from cod liver oil, with potassium permanganate at 0° C., crystallises from alcohol in shining white leaflets melting at 125° C. The above formula is confirmed by the determination of the acetyl value, viz. 355·7 (theory requiring 355). Dihydroxypalmitoleic acid appears to be identical with a dihydroxylated acid obtained by *Ljubarsky*[5] on oxidising the liquid fatty acids from Caspian seal oil.

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[1] *Inaug. Dissert.*, Zürich, 1909.

[2] *Inaug. Dissert.*, Königsberg, 1903.

[3] Fittig, *Liebig's Annal.* 283, 111.

[4] *Berichte*, 1906, 3574.

[5] *Journ. f. prakt. Chem.*, 1898 (57), 26.

It formed with dihydroxystearic acid a molecular compound be in many respects like a chemical individual ("eutectic comp see p. 116) of the composition $C_{17}H_{34}O_4$; it melts at 124°-125° C.

In the light of *Ljubarsky's* and *Bull's* statements the ch individuality of the acid $C_{17}H_{34}O_4$, described by *Fahrion*,[1] m doubted.

DIHYDROXYDIHYDRO-CHAULMOOGRIC ACIDS, $C_{18}H_{34}O_4 = C_{17}$ $(OH)_2.COOH$

Two acids of this composition were obtained by oxidation of moogric acid with potassium permanganate (see p. 205).

DIHYDROXYLATED ACIDS, $C_{18}H_{34}O_2(OH)_2$

(a) DIHYDROXYSTEARIC ACID[2]

Dihydroxystearic acid is best prepared by oxidising or oleic acid with potassium permanganate in alkaline solution ordinary temperature. It forms crystalline laminæ melting at C. (*Saytzeff*), 134° C. (*Albitzky*), 132°-133° C. (*Lewkowitsch*),[3] 132° C. (*Le Sueur*),[4] and solidifying at 119°-122° C. It is com insoluble in water, easily soluble in hot alcohol, less so in the col sparingly soluble in ether.

This dihydroxystearic acid has been resolved into two op active isomerides by means of its strychnine salt[5] (cp. *Grün*, p.

On treatment with potassium permanganate in the hot, pela (nonoic, nonylic), azelaïc, and oxalic acids are obtained, but n stated by *Spiridonoff*,[6] sebacic, suberic, and caprylic acids.

The *calcium*, *zinc*, and *nickel* salts yield, on heating to 165°-1 for twelve hours, considerable quantities (24-34 per cent) of 1 stearic acid, $CH_3(CH_2)_7CO(CH_2)_8COOH$; this confirms indirect constitutional formula given above (p. 178) for oleic acid.

(b) DIHYDROXYSTEARIDIC ACID

On oxidising elaïdic acid with potassium permanganate a dihy acid is obtained differing from the preceding acid by its lower m point, viz. 99°-100° C., and by its greater solubility in alcohol. more easily oxidised in the course of preparation than the iso obtained from oleic acid (*Saytzeff*).[7]

The dihydroxystearic acid melting at 98°-99° C., which was by *Schreiner and Shorey*[1] to be of common occurrence in poor soils, is probably identical with this acid.

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[1] *Journ. Soc. Chem. Ind.*, 1893, 936. Cp. also *Chem. Zeit.*, 1899, 1048. T was described in the second edition of this work (p. 70) as dihydroxyasellic acid.

[2] This acid must not be confounded with natural dihydroxystearic acid; cp.

[3] *Journ. Soc. Chem. Ind.*, 1900, 845.

[4] *Ibid.*, 1901, 1316.

[5] Freundler, *Bull. Soc. Chim.*, 1895 (13), 1052.

[6] Cp. Edmed, *Journ. Chem. Soc.*, 1898, 627.

[7] *Journ. f. prakt. Chem.*, 1883 (33), 315.

(c) p-DIHYDROXYSTEARIC ACID

This acid, obtained from "iso-oleic" acid by oxidation with potassium permanganate, as also by treatment of dibromo-"iso-oleic" acid with silver hydroxide, forms a crystalline powder, melting at 77°-78° C. (*M., K., and A. Saytzeff*),[2] 76°-80° C. (*Grün*),[3] and easily soluble in alcohol and ether. By treatment with potassium iodide, it yields an iodostearic acid which can be reduced to stearic acid by digestion with tin and hydrochloric acid. This acid was described originally by *Saytzeff* as an α-β-dihydroxystearic acid, on the (now disproved) assumption that "iso-oleic" acid had the constitutional formula $C_{15}H_{31}.CH=CH.COOH$.

The true α-β (2, 3) dihydroxystearic acid, $C_{15}H_{31}CH(OH).CH(OH)COOH$, obtained from 2, 3, oleic acid by oxidation with potassium permanganate crystallises (from ethyl acetate) in slender needles melting at 126° C., and is only slightly soluble in alcohol, ether, or acetone in the cold, but appreciably soluble in boiling water (*Le Sueur*,[4] *Ponzio*[5]).

(*d*) A dihydroxystearic acid melting at 122° C. is obtained from petroselinic acid (p. 192) by oxidation with potassium permanganate (*Köhler*).

(*e*) A dihydroxystearic acid, melting at 129·5° C., was produced by oxidising liver lecithin oleic acid (see p. 193) with potassium permanganate (*Hartley*). The acid is soluble in ether, alcohol, acetone, and ethyl acetate and crystallises from all these solvents, generally in form of hexagonal prisms. It is slightly soluble in chloroform and in boiling water (difference from the acid described sub (*a*)). On further oxidation it yields caproic acid (and oxalic acid).

(*f*) A dihydroxystearic acid, melting at 116°-117° C., solidifying at 114°-113° C., is obtained by digesting di-iodostearic acid, derived from ricinoleic acid, with silver hydroxide. *Chonowsky*[6] ascribes to this acid the constitution $CH_3(CH_2)_5.CH(OH).CH_2.CH(OH).(CH_2)_8CO_2H$. It can be readily reduced to stearic acid. The same acid is found amongst the products resulting from the action of concentrated sulphuric acid on ricinoleic acid (see p. 216).

For the several dihydroxystearic acids obtained by the action of concentrated sulphuric acid at 5°-10° C. on ricinoleic acid by *Grün* cp. p. 216.

The 9, 12 *Dihydroxystearic acid*, $CH_3.(CH_2)_5.CH(OH).CH_2.CH_2.CH$

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[1] *Journ. Amer. Chem. Soc.*, 1908, 1599. 1911, 1412. *Unit. St. Dept. Agric., Circ.* 74, Jan. 1913.

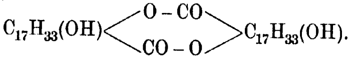
[2] *Journ. f. prakt. Chem.*, 1888 (37), 276.

[3] *Berichte*, 1906, 4400.

[4] *Journ. Chem. Soc.*, 1904, 1712.

[5] *Gazz. chim. ital.*, 1905 (35), ii. 1.

[6] *Berichte*, 1909, 3351.

$(OH)(CH_2)_7COOH$, melts at 69·5°-70° (*Wetterkamp*[1]). On heating, the dihydroxy acid forms a caoutchouc-like mass, which finally becomes viscous, there being formed at first an acid ester of the composition $C_{17}H_{33}(OH)_2.COO.C_{17}H_{33}(OH).COOH$, which is gradually converted into the neutral lactide of dihydroxystearic acid,  $C_{17}H_{33}(OH){<}\begin{matrix}O-CO\\CO-O\end{matrix}{>}C_{17}H_{33}(OH)$. The *sulphuric ester* $CH_3(CH_2)_5.CH(O.SO_3H).CH_2.CH_2.CH(O.SO_3H).(CH_2)_7COOH$ is prepared by the action of chlorosulphonic acid on the 9-12 dihydroxystearic acid. It is readily soluble in water. On heating, it forms inner anhydrides like the 9-12 acid itself.

The *optically active* 9-12 dihydroxystearic acid is obtained in its pure state, melting at 126° C., from the fraction melting at 120° C. (see p. 216) by further re-crystallisation. A preparation, the optical activity of which has, however, not been tested, was found to be insoluble in petroleum ether, ether, and cold alcohol, and only sparingly soluble in hot alcohol. The solution had an acid reaction. The acid exhibited the property, characteristic of all hydroxy acids, to be converted, by prolonged heating above its melting point, into a syrupy mass containing anhydrides.

For the natural dihydroxystearic acid melting at 141°-143° C. cp. p. 221.

DIHYDROXYJECOLEIC ACID, $C_{19}H_{38}O_4 = C_{19}H_{36}O_2(OH)_2$

This acid, stated to have been obtained by oxidising the liquid cod liver oil fatty acids with a half-saturated solution of potassium permanganate at 0° C. (*Heyerdahl*), is in *Bull's*[2] opinion probably a "eutectic" mixture of derivatives of oleic and gadoleic acids. The melting point is given by *Heyerdahl* as 114°-116° C.

DIHYDROXYGADOLEIC ACID, $C_{20}H_{40}O_4 = C_{20}H_{38}O_2(OH)_2$

On oxidising gadoleic acid (p. 194) with an alkaline solution of potassium permanganate at 0° C., dihydroxygadoleic acid crystallising from alcohol in lustrous white crystals, melting at 127·5°-128° C. (*Bull*[2]) is said to be obtained.

DIHYDROXYLATED ACIDS, $C_{22}H_{42}O_2(OH)_2$

(*a*) DIHYDROXYBEHENIC ACID

This acid, obtained by oxidising erucic acid with potassium permanganate, forms granular crystals melting at 132°-133° C. 132°-

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[1] Grün and Wetterkamp, *Farben-Zeitung*, 1909, 279. Wetterkamp, *Inaug. Dissert.*, Zürich, 1909.

[2] *Berichte*, 1906, 3575.

133·5° C. (*H. Meyer and R. Beer*[1]). It dissolves readily in warm alcohol, but is insoluble in cold ether.[2]

(*b*) Isodihydroxybehenic Acid[3]

Isodihydroxybehenic acid prepared from brassidic acid by oxidation with potassium permanganate, melts at 99°-100° C., and solidifies at 88°-87° C.

(*c*) Para-dihydroxybehenic Acid[4]

This third isomeride prepared from "isoerucic" acid, melts at 86°-88° C., and solidifies at 82°-80° C.

3. Trihydroxylated Acids, $C_{18}H_{33}O_2(OH)_3$

Trihydroxylated acids are obtained by oxidising ricinoleic and ricinelaïdic acids respectively with potassium permanganate. Three acids have been described hitherto (*Hazura and Grüssner*[5]); two are derived from ricinoleic, and the third from ricinelaïdic acid. *Mangold* showed that ricinelaïdic acid also yields two trihydroxylated acids, one of which is certainly identical with that prepared by *Hazura and Grüssner*. It should be pointed out that by oxidising the methylester of ricinoleic acid with potassium permanganate *Haller* obtained only one trihydroxystearic ester, melting at 87° C.

(*a*) Trihydroxystearic Acid

This acid obtained from ricinoleic acid together with the following acid (*b*), crystallises from hot water in microscopic needles melting at 140°-142° C. It is insoluble in cold, and dissolves with difficulty in hot water, as also in cold alcohol and ether. Warm alcohol and glacial acetic acid dissolve it readily. Trihydroxystearic acid is insoluble in carbon bisulphide, chloroform, benzene, and petroleum ether. Probably this acid is optically active.[6]

(*b*) 9, 10, 12 Trihydroxystearic Acid

This acid differs from the preceding one by its lower melting point, viz. 110°-111° C., and by its ready solubility in ether and benzene. The acid is optically active;[6] $[\alpha]_D = -6{\cdot}25°$ in glacial acetic acid ($c = 10$). By prolonged heating to 115°-120° C. the acid is converted into a viscous substance which represented, after purification, an inner anhydride of the formula $(C_{18}H_{34}O_4)_2$.

[1] *Mitt. d. K. K. Akad. d. Wiss.*, Vienna, January, 1912.

[2] Hazura and Grüssner, *Monatsh. f. Chem.*, 1888 (9), 948. Cp. also Albitzky, *Chem. Centralbl.*, 1899, i. 1068.

[3] Saytzeff, *Journ. f. prakt. Chem.*, 1894 (50), 82; Albitzky, *Chem. Centralbl.*, 1899, i. 1068.

[4] Alexandroff and Saytzeff, *Journ. f. prakt. Chem.*, 1894 (49), 63.

[5] Cp. also Dieff, *Journ. f. prakt. Chem.*, 1889 (39), 339.

[6] Walden, *Berichte*, 1894, 3475.

The *sulphuric ester*, $CH_3(CH_2)_5CH(OSO_3H)CH_2CH(OSO_3H).CH(OSO_3H_2)(CH_2)_7COOH$, obtained by the action of chlorosulphonic acid, is soluble in water. On heating the aqueous solution, sulphuric acid is split off and a condensation product is obtained which appears to be formed of three molecules of trihydroxystearic acid. The condensation product has very likely the following composition, $C_{17}H_{32}(OH)_3CO.O.C_{17}H_{32}(OH)_2CO.O.C_{17}H_{32}.(OH)_2COOH$.

(c) ISOTRIHYDROXYSTEARIC ACID

Two isomerides are obtained, according to *Mangold*,[1] by oxidising ricinelaïdic acid. One of these was described by *Hazura and Grüssner* as melting at 114°-115° C., sparingly soluble in hot water, ether, chloroform, and petroleum ether, and dissolving readily in alcohol. Probably *Mangold's* acid, of the melting point 113°-116° C., is identical with isotrihydroxystearic acid.

The second trihydroxystearic acid from ricinelaïdic acid melts between 117° and 120° C.

It appears probable that both acids rotate the plane of polarised light.

4. Tetrahydroxystearic Acid, $C_{18}H_{32}O_2(OH)_4$

The tetrahydroxystearic—*sativic*—acid obtained by *Hazura* on oxidising linolic acid, crystallises from water in microscopic needles or pyramidal prisms melting at 173° C. (*Hazura*), 174° C. (*Hehner and Mitchell*). One part of the acid is soluble in 2000 parts of boiling water. Sativic acid is insoluble in cold water, ether, chloroform, carbon bisulphide, and benzene. Hot alcohol and glacial acetic acid dissolve it readily. Potassium permanganate oxidises it to azelaïc acid, oxalic acid, and a hexoic (caproic ?) acid (*Goldsobel*[2]).

Several observers[3] obtained by the same method tetrahydroxy acids of lower melting points (152° C.; 157°-158° C.; 161° C.; 165° C.). Since theory predicts the existence of a number of isomeric tetrahydroxy acids, the author considered it likely that at least two isomeric tetrahydroxystearic acids existed.[4] Since then, indications as to their existence seemed to have been furnished by the fact that *Hartley*[5] obtained two apparently different tetrahydroxy acids by oxidising the liquid fatty acids of liver fat. One of these acids melted after repeated crystallisation at 175° C., and yielded on further oxidation with potassium permanganate volatile acids (acetic, caproic).

This view appeared to be further confirmed by observations of *Tsujimoto*,[6] who obtained from chrysalis oil, soya bean oil, and rice oil, tetrahydroxystearic acids melting respectively at 154° C., 156°-157·5° C., and 159° C.

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[1] *Monatsh. f. Chem.*, 1892, 326.

[2] *Chem. Zeit.*, 1906, 825.

[3] Fahrion, *Zeits. f. angew. Chem.*, 1904, 1483; Power and Barrowcliff, *Journ. Chem. Soc.*, 1905, 896; Krźiźan, *Chem. Revue*, 1908, 8; 1909, 3.

[4] See 4th edition of this work, Vol. I. p. 177; *Jahrbuch d. Chem.*, 1909, xix. 43.

[5] *Journ. f. Physiol.*, 1909 (38), 367.

[6] *Chem. Revue*, 1911, p. 111.

The view that the lower melting point of some preparations of sativic acid might be due to small proportions of adhering dihydroxystearic acid was disproved by *H. Meyer and R. Beer*,[1] who by careful purification of a tetrahydroxystearic acid melting at 158°, only succeeded to raise its melting point to about 163° C. They therefore arrive at the conclusion that two isomeric sativic acids exist, melting respectively at 173° C. and 162°-163° C. The lower melting acid is termed *α-sativic acid,* the term β-sativic acid being reserved to the higher melting acid. α-sativic acid is more readily soluble in water than the higher melting β-acid. The two acids would therefore appear to correspond to two linolic acids. This finds support in a statement by *Thoms*, who obtained from telfairic acid a tetrahydroxy acid melting at 177° C.

5. Hexahydroxystearic Acids, $C_{18}H_{30}O_2(OH)_6$

(*a*) Linusic Acid [2]

Linusic acid, obtained by the oxidation of linolenic acid, crystallises from water in rhombic plates (occasionally in needles) melting at 203°-205° C. (*Hazura*), 204·5° C. (*Kržižan*). Linusic acid is more readily soluble than sativic acid in water; it is insoluble in ether, and sparingly soluble in alcohol.

(*b*) Isolinusic Acid [2]

This isomeride was first obtained, together with linusic acid, by oxidising linseed oil fatty acids with potassium permanganate. From this acid the existence of isolinolenic acid (p. 209) was inferred.

Isolinusic acid crystallises in prismatic needles melting at 173°-175° C. (*Hazura*), 176° C. (*Kržižan*). It is sparingly soluble in cold water, and dissolves easily in hot water and hot alcohol; it is insoluble in ether, benzene, carbon bisulphide, and chloroform.

Bedford doubted the existence of this acid (cp. p. 233). The statements of *Tsujimoto* and *Kržižan*, who obtained isolinolenic acid from chrysalis oil, and from raspberry and blackberry seed oils, respectively, would not, in the author's opinion, have controverted *Bedford's* statement, inasmuch as in each case the "isolinusic" acid was only identified by its melting point, which is the same as that of β-sativic acid. But since *Rollett* has shown that linolenic acid prepared from hexabromolinolenic acid yields on oxidation linusic as well as isolinusic acid, the existence of isolinusic acid can no longer be doubted.

6. Octohydroxylated Acids, $C_nH_{2n-8}O_2(OH)_8$

Acids of this composition should be obtained by very careful oxidation of the acids belonging to the clupanodonic series. Clupanodonic acid itself, although readily accessible, has not yet been examined in this direction. The existence of a higher octohydroxylated acid should, however, point to the possibility of preparing octohydroxystearic acid.

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[1] *Monatsh. f. Chem.*, 1892, 326.

[2] Reformatzky, *Journ. f. prakt. Chem.*, 1890 (41), 529, threw doubt on the existence of these acids.

OCTOHYDROXYARACHIDIC ACID, $C_{20}H_{40}O_{10} = C_{20}H_{32}O_2(OH)_8$

This acid was found amongst the oxidation products of the unsaturated acids of liver lecithin (*Hartley*[1]). It is easily soluble in water and crystallises from it in small rectangular prisms, melting at 195° C.

II.—ACIDS OF THE STEAROLIC SERIES, $C_nH_{2n-4}O_2$

These acids are isomeric with the acids of the "Linolic Series." They differ from them in that they contain one pair of trebly linked carbon atoms. They are also isomeric with the acids of the "Tariric Series," with which they share the property of having one triple bond.

The acids belonging to this series are obtained from the dibromo derivatives of the acids of the "Oleic Series" by heating with (methyl- or ethyl-) alcoholic potash, whereby two HBr groups are eliminated.

These acids are very stable and are not oxidised by exposure to the atmosphere, like linolic acid. On treatment with *chlorine* or *bromine*, one molecule of the halogens is easily assimilated. The second molecule is only absorbed, if the halogens be allowed to act for a prolonged time and the action be assisted by heat or by exposure to daylight. The absorption of *iodine* is much slower than that of chlorine and bromine; even if ferrous iodide be used as a catalyst, the amount of iodine absorbed does not exceed one molecule.[2] By allowing iodine to act in a solution of glacial acetic acid, and heating to 50° or 60° C. with agitation, the di-iodides are formed rapidly and quantitatively.

Even if *Hübl's* reagent be used (on stearolic and behenolic acids), only one molecule of iodo-chloride is absorbed. *This behaviour forms a characteristic difference between these acids and the isomeric acids of the linolic series.* (The same characteristic difference exists between the glycerides of stearolic and behenolic acids on the one hand, and linolin on the other.)

Molinari's statement that stearolic acid does not assimilate ozone and can thus be easily differentiated from the acids of the linolic series, is strongly contested as erroneous by *Harries*,[3] but is quite as strenuously maintained by *Molinari*.[4]

PALMITOLIC ACID, $C_{16}H_{28}O_2 = CH_3.(CH_2)_7.C{\equiv}C.(CH_2)_5.COOH$

Palmitolic acid (not to be confounded with palmitoleic acid, p. 177) obtained by heating hypogæic dibromide with alcoholic potash to 170° C. (*Schröder*[5]), crystallises in silky needles melting at 42° C. (47° *Bodenstein*[6]). It boils under 15 mm. pressure at 240° C. It is insoluble in water, easily soluble in alcohol and ether, and absorbs readily two and four atoms respectively of bromine. After treatment with fuming nitric acid the following oxidation products were identified: Palmitoxylic acid ($C_{16}H_{24}O_4$), suberic acid, and suberic aldehyde. By treatment with concentrated sulphuric acid keto-palmitic acid, $CH_3.(CH_2)_7.CO.(CH_2)_6CO_2H$, melting at 74° C., is obtained.

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[1] *Journ. f. Physiol.*, 1909 (38), 367.

[2] Liebermann and Sachse, *Berichte*, 1891, 4112; Quensell, *ibid.*, 1909, 2441.

[3] *Berichte*, 1907, 4907.

[4] *Berichte*, 1908, 595; 2782.

[5] *Liebig's Annal.*, 1867 (143), 27.

[6] *Berichte*, 1894, 3402.

STEAROLIC ACID, $C_{18}H_{32}O_2 = CH_3 - (CH_2)_7 - C \equiv C(CH_2)_7 - COOH$

Stearolic acid is obtained by heating oleic dibromide with alcoholic potash (*Overbeck*,[1] *Quensell*[2]). The several glycerides (mono-, di-, tri-) prepared synthetically from this acid have been described above (p. 29). It crystallises from alcohol in long white prisms melting at 48° C.

The comparatively high melting point had induced the author to prepare it commercially from oleic acid with a view to using it as candle material (cp. Vol. III. Chap. XV. "Conversion of Oleic Acid into Candle Material").

Stearolic acid (like tariric acid) seems to absorb hydrogen *in statu nascendi* with difficulty. *Arnaud*[2] reduced stearolic acid to stearic acid by means of fuming hydriodic acid and amorphous phosphorus. There is little doubt that reduction with hydrogen in the presence of catalyst would readily yield stearic acid.

By oxidising stearolic acid with nitric acid, pelargonic and azelaïc acids are obtained. Oxidation with potassium permanganate yields as principal products pelargonic and suberic acids. Caprylic and azelaïc acids represent only 25 per cent of the resulting substances (*Arnaud and Hasenfratz*[3]). By careful oxidation stearoxylic acid is obtained. On melting with caustic potash, acetic, hypogæic, and, finally, myristic acids are obtained (*Marasse*,[4] *Bodenstein*[5]).

Concentrated sulphuric acid yields with stearolic acid 10, ketostearolic acid (*Baruch*[6]).

Stearolic acid absorbs two molecules of hydriodic acid when a current of hydriodic acid gas is passed through the melted acid; the di-iodo-stearic acid so obtained can be reduced to stearic acid, whilst the addition product obtained when allowing only one molecule of hydriodic acid to be absorbed, yields, by reduction with zinc and acetic acid, elaïdic acid. By boiling the addition product from one molecule of hydrioidic acid and one molecule of stearolic acid, the original stearolic acid is regenerated, whereas the product from two molecules of hydriodic acid and one molecule of stearolic acid yields a complex mixture containing regenerated stearolic acid and two isomerides having triple bonds respectively between the 8th and 9th carbon atoms and between the 10th and 11th carbon atoms. Nitric acid oxidises the former of the two acids to suberic acid, and the latter to sebacic acid.

Stearolic di-iodide, $C_{18}H_{32}O_2I_2$, was obtained by allowing iodine in carbon bisulphide solution to act on stearolic acid, ferrous iodide being used as a catalyst (*Liebermann and Sachse*[7]). The iodide is formed almost instantaneously by employing ***Arnaud and Posternak's***[1] method, the theoretical quantity of iodine being allowed to act in glacial acid solution on the acid at a temperature of 50°-60° C. with agitation. The di-iodide crystallises from strong alcohol in colourless needles and from somewhat dilute alcohol in plates melting at 51° C. The *ammonium salt* is easily soluble in cold alcohol (Difference from tariric acid).

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[1] *Liebig's Annal.*, 1866 (140), 49.
[2] *Compt. Rend.*, 1896 (122), 1000.
[3] *Compt. rend.*, 1911 (152), 1603.
[4] *Berichte*, 1869, 259.
[5] *Berichte*, 1894, 3398.
[6] *Berichte*, 1894, 174.
[7] *Berichte*, 1891, 4116.

Methylester, crystallises in needles solidifying at $-3°$ C., and distils under a pressure of 20 mm. at 204°-206° C.

Ethylester, distils under a pressure of 20 mm. at 215°-216° C.

Amide, crystallises in scales melting at 78° C.

Anilide, crystallises in prisms melting at 63° C.

PETROSELINOLIC ACID, $C_{18}H_{32}O_2 = CH_3.(CH_2)_{10}C = C(CH_2)_4COOH$

This acid, the constitutional formula of which is assumed (by the author) to correspond to that of petroselinic acid, was prepared by melting petroselinic dibromide with alcoholic potash under pressure (see p. 193). The acid melts at 45° C. (*E. Vongerichten and A. Köhler*[2]).

BEHENOLIC ACID, $C_{22}H_{40} = O_2CH_3 - (CH_2)_7 - C \equiv C - (CH_2)_{11} - COOH$

This acid, obtained from erucic dibromide in the same manner as is stearolic acid from oleic dibromide (cp. *Otto*,[3] *Hausknecht*,[4] *v. Grossmann*,[5] *Holt*;[6] *Quensell*[7]), crystallises from alcohol in shining needles, melting at 57·5° C. The several glycerides (mono-, di-, tri-) containing this acid have been described above.

Behenolic acid absorbs readily two and four atoms of bromine, forming respectively dibromide and tetrabromide. With zinc dust and glacial acetic acid it is reduced to brassidic acid. Fuming nitric acid oxidises it to dioxybehenolic, brassidic, $C_{22}H_{40}O_4$, brassylic, $C_{13}H_{24}O_4$, pelargonic, and arachidic acids, with evolution of carbon dioxide (*Grossmann*). By treatment with concentrated sulphuric acid keto-behenic acid, $C_8H_{17}CO.(CH_2)_{12}COOH$, is obtained.[5]

Behenolic di-iodide, $C_{22}H_{40}I_2O_2$, is obtained by allowing the theoretical amount of iodine to act on a glacial acetic acid solution of behenolic acid at a temperature of 50°-60° C. It crystallises from hot alcohol in soft needles, melting at 50°-51° C. (*Arnaud and Posternak*[8]).

III.—ACID OF THE RICINSTEAROLIC SERIES, $C_{18}H_{31}(OH)O_2$

RICINSTEAROLIC ACID, $C_{18}H_{32}O_3 = CH_3.(CH_2)_5.CH(OH).CH_2 - C \equiv C(CH_2)_7.COOH$

Ricinstearolic acid, obtained from ricinoleic dibromide in the same manner as is stearolic acid from oleic dibromide (*Ulrich*,[9] *Goldsobel*;[10]

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[1] *Compt. rend.*, 1909 (149), 220.
[2] *Berichte*, 1909, 1638.
[3] *Liebig's Annal.*, 1865 (135), 226.
[4] *Ibid.*, 1867 (143), 41.
[5] *Inaug. Dissert.*, Leipzig, 1890. *Berichte*, 1893, 641.
[6] *Inaug. Dissert.*, Rostock, 1892.
[7] *Inaug. Dissert.*, Berlin, 1909.
[8] *Compt. rend.*, 1909 (149), 221.
[9] *Zeit. f. Chem.*, 1867, 547.
[10] *Berichte*, 1894, 3122.

Mangold[1]), crystallises from alcohol in needles melting at 51° C. (*Ulrich*); 53° C. (*Quensell*[2]).

The acid is optically active $\alpha[_D] = +13{\cdot}67°$ in acetone solution (for $c = 6{\cdot}4$) (*Walden*[3]).

Treatment with concentrated sulphuric acid leads to ricinostearoxylic acid (ketohydroxystearic acid), $C_{18}H_{34}O_4$.

The *sulphuric ester*, $CH_3(CH_2)_5.CH(O.SO_3H).CH_2.C \equiv C.(CH_2)_7$ COOH, is obtained from chlorosulphonic acid and ricinstearolic acid (*Woldenberg*[4]).

IV.—Dibasic Acids

These acids are soluble in water, and are therefore easily isolated. Their characteristic melting points afford a ready means of identification.[5]

Suberic Acid, $C_8H_{14}O_4 = C_6H_{12}(COOH)_2$

Suberic acid crystallises from water in long needles or irregular plates melting at 140° C.; it boils *in vacuo* at 152·5° C., and under a pressure of 15 mm. at 230° C.

The acid is almost insoluble in chloroform. 100 parts of ether dissolve at 15° C. 0·809 part; 100 parts of water dissolve at 0°, 15·5°, 20°, 50°, 65° C.—0·08, 0·142, 0·16, 0·98, 2·2 parts respectively.

Azelaïc Acid, $C_9H_{16}O_4 = C_7H_{14}(COOH)_2$

This acid is one of the decomposition products of oleic acid ozonide and linolic acid ozonide, as also of the nitrogen tetroxide addition compound of oleic and ricinoleic acids. It crystallises from water in large laminæ or long flat needles, melting at 106·2° C.; it boils *in vacuo* at 158° C., and under a pressure of 15 mm. at 237° C.

100 parts of ether dissolve at 11° C. 1·88 parts, and at 15° C. 2·68 parts of the acid. 100 parts of water dissolve at 0°, 20°, 50°, 65° C.—0·10, 0·24, 0·82, 2·22 parts respectively. *Molinari and Fenaroli*[6] give the following solubilities: 100 parts of water dissolve at 15°, 22°, 44·5°, and 55° C. respectively the following amounts:—0·212, 0·214, 1·017, 1·648 parts; at higher temperatures the solubilities increase rapidly.

Sebacic Acid, $C_{10}H_{18}O_4 = C_8H_{16}(COOH)_2$

Sebacic acid was recognised by *Redtenbacher*[7] as a characteristic product formed by destructive distillation of oils and fats. It forms a decomposition product of the nitrogen tetroxide addition compound of isoleic acid. Sebacic acid crystallises from water in thin laminæ, melts at 133°-133·5° C., and boils *in vacuo* at 164° C., and under a pressure of 15 mm. at 243·5° C. It is easily soluble in alcohol and ether. 100 parts of water dissolve at 0°, 20°, 50°, 65° C.—0·004, 0·10, 0·22, 0·42 parts respectively.

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[1] *Monatshefte*, 1895 (15), 314.

[2] *Inaug. Dissert.*, Berlin, 1909.

[3] *Berichte*, 1894, 3475.

[4] *Inaug. Dissert.*, Zürich, 1908.

[5] Cp. Bouveault, *Bull. Soc. Chim.*, 1898, 562.

[6] *Berichte*, 1908, 2790.

[7] *Liebig's Annal.*, 1840 (35), 190.

BRASSYLIC ACID, $C_{13}H_{24}O_4 = C_{11}H_{22}(COOH)_2$

Brassylic acid is obtained from erucic acid as one of the decomposition products of its ozonide or its nitrogen tetroxide addition product (*Jegorow*); it is also formed by oxidation of behenolic acid with fuming nitric acid. It crystallises from hot aqueous solutions in flat needles, melting at 112°,[1] 114° C.[2]; the acid is easily soluble in alcohol and ether, insoluble in petroleum ether and cold benzene; 100 parts of water dissolve at 24° C. 0·74 parts.

B. ALCOHOLS

I.—ALCOHOLS OF THE ETHANE SERIES, $C_nH_{2n+2}O$

The alcohols belonging to the saturated series occur in waxes, or in the wax-like "unsaponifiable" constituents of some fats and are solid, white, crystallisable substances, melting without decomposition. They are not acted upon by dilute alkalis or acids; on boiling with alcoholic potash and diluting the solution with water, they are precipitated unchanged. Hence they are termed "unsaponifiable."

On heating the alcohols with organic acids (or their chlorides or anhydrides) esters are formed with elimination of water.

The alcohols dissolve in concentrated sulphuric acid in the cold to form alkyl sulphuric acids; on boiling with dilute acids they are resolved into their components (cp. Chap. IX.).

A characteristic property of the alcohols, used for their identification, is their behaviour with soda-lime (or potash-lime) on heating; they are thereby converted into the corresponding fatty acids, with evolution of hydrogen. Thus cetyl alcohol yields palmitic acid, as is indicated by the equation—

$$C_{15}H_{31}.CH_2.OH + NaOH = C_{15}H_{31}.COONa + 2H_2.$$

On oxidation with chromic acid in acetic acid solution, they yield fatty acids having the same number of carbon atoms.

These reactions are employed for the identification and quantitative determination of these alcohols (Chap. IX.).

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[1] Grossmann, *Berichte*, 1893, 644.

[2] Fileti and Ponzio, *Gazz. chim.*, 1893 (23), ii. 393.

PISANGCERYL ALCOHOL, $C_{13}H_{28}O$ [1]

Pisangceryl alcohol is stated to be the alcoholic constituent of pisang wax; it melts at 78° C. The uneven number of carbon atoms would seem to suggest that the identity of this alcohol requires confirmation.

CETYL ALCOHOL, $C_{16}H_{34}O$

Cetyl alcohol, or ethal (first isolated by *Chevreul*), occurs, combined with palmitic acid, in spermaceti. It has also been found in the sebaceous glands of geese and ducks. It is a white, tasteless, and odourless crystalline mass melting at 50° C. and boiling under ordinary pressure at 344° C. without decomposition, under a pressure of 15 mm. at 189·5° C., *in vacuo* at 119° C. $d^{49·5°}_{4°} = 0·8176$; $d^{60°}_{4°} = 0·8105$; $d^{79·7°}_{4°} = 0·7984$; $d^{98·7°}_{4°} = 0·7837$.

Cetyl alcohol is insoluble in water; it dissolves in alcohol, and is very easily soluble in ether and in benzene. The statement that cetyl alcohol, when heated with an aqueous solution of potassium bichromate and dilute sulphuric acid, is converted into cetyl aldehyde crystallising from alcohol and ether in lustrous laminæ is incorrect, as cetyl alcohol remains for the most part unchanged; in acetic acid solution, however, the oxidising mixture converts cetylalcohol into palmitic acid.[2] Cetyl alcohol dissolves in cold concentrated sulphuric acid to form cetyl sulphuric acid, $C_{16}H_{33}O.SO_3H$, which by boiling with aqueous hydrochloric acid is split into sulphuric acid and cetyl alcohol.[3]

Cetyl acetate crystallises in needles melting at 22°-23° C., and boiling at 199·5°-200·5° C. under a pressure of 15 mm. It dissolves sparingly in alcohol.

Cetyl benzoate crystallises in scales melting at 30° C.; it is readily soluble in ether, and dissolves with difficulty in alcohol.

OCTODECYL ALCOHOL, $C_{18}H_{38}O$

This alcohol occurs, as an ester, in spermaceti and in rump gland wax. It crystallises in large silvery laminæ (from alcohol) melting at 59° C., and boiling at 210·5° C. under 15 mm. pressure; if the pressure is allowed to rise to 100 mm. it undergoes decomposition. $d^{59°}_{4°} = 0·8124$, $d^{70}_{4°} = 0·8048$, and $d^{99·1°}_{4°} = 0·7849$.

Octodecyl acetate melts at 31° C., and boils at 222°-223° C. under a pressure of 15 mm.

ALCOHOLS, $C_{20}H_{42}O$

(*a*) *Arachyl Alcohol.*—This alcohol is a constituent of the fat of the dermoid cysts, and hitherto has been considered to be identical with cetyl alcohol. The alcohol melts at 70° C.; on oxidation with chromic acid it yields arachidic acid. Arachyl alcohol prepared from arachidic acid (*Haller*) melts at 71° C.

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[1] Greshoff and Sack, *Rec. d. trav. chim. Pays-Bas*, 1901, 65.

[2] Cp. Claus and v. Dreden, *Journ. f. prakt. Chem.*, 1891 (43), 148; with regard to cetylphosphate, cp. Biehringer, *Berichte*, 1905, 3974.

[3] Cochenhausen, *Dingl. Polyt. Journ.*, 1897 (303), 284.

Arachyl acetate melts at 44° C. and boils under a pressure of 3 mm. at 22° C. (*Ameseder*[1]).

(*b*) *Raphia Alcohol.*—This alcohol forms the chief constituent of Raphia Ruffia wax (Vol. II. Chap. XIV.). It is not identical with the arachyl alcohol obtainable from arachidic acid (*Haller*[2]). The alcohol melts at 80° C. The *acetate* melts at 55° C.; the *benzoate* melts at 55° C.

CARNAÜBYL ALCOHOL, $C_{24}H_{50}O$

Carnaübyl alcohol, stated by *Darmstaedter and Lifschütz* to occur in wool wax,[3] is obtained from its alcoholic solution (75 to 80 per cent alcohol) in crystals melting at 68°-69° C., solidifying at 67°-65° C. The alcohol is said to retain water very tenaciously and to form a tallow-like mass, consisting of 26·7 per cent of carnaübyl alcohol and 73·3 per cent of water. On exposure to the air this mass does not lose weight.

By oxidation with chromic acid, carnaübic acid is obtained.

Doubt has been thrown on the existence of this alcohol by *Röhmann*. This doubt would seem to be supported by an observation made by *Matthes and Sander*,[4] who found in the unsaponifiable matter of laurel oil a crude alcohol solidifying in a one per cent alcoholic solution to a gelatinous mass exhibiting (after drying) a melting point of 65°-66° C., which rose to 67°-68° C. after repeated redissolving in alcohol. This property, taken in conjunction with the results of elementary analysis, would seem to point to the substance being carnaübyl alcohol; yet by recrystallising from petroleum ether, the gelatinous mass could be resolved into pure melissyl alcohol and laurane (a hydrocarbon, melting at 69° C.).

An alcohol of the formula, $C_{24}H_{50}O$ or $C_{25}H_{52}O$, has been found in small quantities in beeswax.

CERYL ALCOHOL, $C_{26}H_{54}O$

Ceryl alcohol occurs as ceryl cerotate in Chinese wax, and as ceryl palmitate in opium wax. In ordinary beeswax it occurs to a small extent only, whereas it forms the only alcoholic constituent of Ghedda wax.[5] In wool fat it is found in its free state,[6] and occurs perhaps also as ceryl cerotate therein.[7] Very small quantities of ceryl alcohol have been found in the unsaponifiable matter of Japan wax. It has also been identified as a constituent of the wax of flax[1] and of carnaüba wax.

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[1] *Zeits. f. phys. Chem.*, 1907 (52), 121.

[2] *Compt. rend.*, 1907 (144), 594.

[3] *Berichte*, 1896 (29), 2890; *Journ. Soc. Chem. Ind.*, 1897, 150.

[4] *Arch. d. Pharm.*, 1908 (246), 169.

[5] A. Lipp and E. Kuhn, *Journ. f. prakt. Chem.*, 1912 (86), 184.

[6] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 138.

[7] Buisine, *Bull. Soc. Chim.*, 1887 (72), 201.

It crystallises readily from an alcoholic solution in crystals melting at 79° C. and undergoing decomposition on distillation. By heating ceryl alcohol with soda-lime cerotic acid is obtained.

Ceryl alcohol behaves with concentrated sulphuric acid like cetyl alcohol.

Ceryl acetate melts at 65° C.

Ceryl benzoate melts at 53·5° C. (*Lipp and Kuhn*).

ISOCERYL ALCOHOL, $C_{27}H_{56}O$

This alcohol is stated to have been found in the wax of *Ficus gummiflua* and to melt at 62° C.; its acetate melts at 57° C.

An alcohol,[2] stated to have the formula $C_{27}H_{56}O + 6H_2O$, was isolated from wool fat by *Darmstaedter and Lifschütz*. The existence of this alcohol must be doubted.

MELISSYL ALCOHOL (MYRICYL ALCOHOL), $C_{30}H_{62}O$ [3]

Melissyl alcohol occurs in beeswax as palmitate (*Brodie*), in carnaüba wax both in the free state and as an ester (*Storey-Maskelyne*,[4] *Pieverling*,[5] *Stürcke*[6]), in sugar cane wax[7] and in curcas wax (see Vol. II. Chap. XIV.) as melissyl melissate. Many oils and fats seem to contain very small quantities of this alcohol. Thus it has also been found in parsley seed oil and in Japan wax; laurel oil contains about 0·125 per cent.

Melissyl alcohol crystallises from ether in small silky needles melting at 85° C. or 88° C. (*Gascard*). It is almost insoluble in cold, but dissolves readily in hot alcohol; it is sparingly soluble in cold petroleum ether, common ether, and chloroform; in the hot it dissolves much more readily in these solvents. By heating with soda-lime the alcohol is converted into melissic acid. According to *Schwalb*,[8] "myricyl" alcohol from beeswax has the formula $C_{31}H_{64}O$. *Gascard*[9] states that the "myricyl" alcohols from beeswax and carnauba wax are identical, and have the composition $C_{31}H_{64}O$. The analytical data obtained by *Matthes and Sander*[10] agree, however, with the formula $C_{30}H_{62}O$.

Melissyl acetate melts at 73° C. (*Gascard*), 75° C. (*Matthes and Sander*).

Melissyl benzoate melts at 70° C. (*Gascard*; *Matthes and Sander*).

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[1] Cross and Bevan, *Journ. Chem. Soc.*, 1890, 196.

[2] *Berichte*, 29, 2895.

[3] Gascard gives the formula $C_{31}H_{64}O$ (cp. *Journ. Soc. Chem. Ind.*, 1893, 955).

[4] *Journ. Chem. Soc.* 7 87.

[5] *Liebig's Annal.* 183, 344.

[6] *Ibid.* 223, 283.

[7] The wax obtained by scraping off the sugar cane is almost pure myricyl alcohol, Wijnberg. *Het Rietwas, etc.*, Amsterdam, 1909 (I. H. de Bussy).

[8] *Liebig's Annal.* 235, 126.

[9] *Journ. Pharm. Chem.*, 1893, 49.

[10] *Arch. d. Pharm.*, 1908 (246), 169.

PSYLLOSTEARYLIC ALCOHOL, $C_{33}H_{68}O$[1]

This alcohol, first described as having the composition $C_{33}H_{66}O$, later on judged to be an anhydride of the formula $(C_{33}H_{66}O)_2O$, has been recognised as an alcohol having the composition $C_{33}H_{68}O$. The uneven number of carbon atoms would, however, suggest that the formula $C_{33}H_{68}O$ requires confirmation. The alcohol is stated to occur combined with psyllostearylic acid (psyllic acid) in the wax of *Psylla alni* (an aphide living on the leaves of *Alnus incana*), and also in the wax of humble (bumble) bees (*Sundwick*[2]); it crystallises in silky scales from benzene, petroleum ether, and chloroform. The psylla wax alcohol melts at 68°-70° C., the humble (bumble) bee wax at 69°-69·5° C. Nevertheless the two alcohols are not identical, for *Sundwick*[2] has shown later on that psylla alcohol yields psyllostearylic acid on heating with soda-lime, whereas humble (bumble) bee wax yields a different product.

Psyllostearyl acetate, $C_{33}H_{67}O.C_2H_3O$ crystallises in needles.

Psyllostearyl benzoate, $C_{33}H_{67}O.C_7H_5O$, crystallises from benzene or petroleum ether in needles, melting at 68°-69° C.

An alcohol of the same composition occurs to the extent of about 30 per cent in the crude sugar cane wax (*Wijnberg*).

INCARNATYL ALCOHOL, $C_{34}H_{70}O$

This alcohol has been isolated[3] from the flowers of *Trifolium incarnatum*, L. It crystallises in fine, colourless needles melting at 72°-74° C., and has been identified with an alcohol isolated by *Sundwick*[4] from the wax of the humble (bumble) bee, and stated to melt at 75° C. (It will be seen from the above given notes that the composition and melting point of humble bee wax is somewhat doubtful.)

II.—ALCOHOLS OF THE ALLYLIC SERIES,[5] $C_nH_{2n}O$

The alcohols belonging to this group, and stated to occur in waxes, have not yet been studied thoroughly.

LANOLIN ALCOHOL, $C_{12}H_{24}O$

This alcohol had been stated by *Marchetti*[6] to occur in wool wax. Shortly afterwards *Darmstaedter and Lifschütz*[7] isolated from wool wax two more alcohols, to which the formulæ $C_{10}H_{20}O$ and $C_{11}H_{22}O$

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[1] Sundwick, *Zeits. f. physiol. Chem.*, 1901 (32), 355; *Zeits. f. physiol. Chem.*, 1907 (53), 364.

[2] *Ibid.*, 1911 (72), 455.

[3] H. Rogerson, *Journ. Chem. Soc.*, 1910, 1011.

[4] *Zeits. f. physiol. Chem.*, 1898 (26), 58.

[5] The unsaturated alcohols occurring in sperm oil (Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 134) probably belong to this series.

[6] *Gazz. chim.*, 1895, 22.

[7] *Journ. Soc. Chem. Ind.*, 1896, 206.

were assigned. Believing to have found lower homologues of lanolin alcohol, they proposed the name "Lanestols" for the whole series. More accurate examination undertaken by them in consequence of *Lewkowitsch's* researches[1] proved, however, that the two alcohols, $C_{10}H_{20}O$ and $C_{11}H_{22}O$, do not exist. Therefore, the existence of *Marchetti's* alcohol also becomes doubtful.

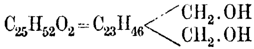
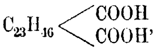
An alcohol of the composition $C_{15}H_{30}O$ has been found in the ether-soluble part of the wax from *Ficus gummiflua.* An alcohol of the formula $C_{36}H_{72}O$ is stated to occur, combined with acids, in the wax of cochineal.

III.—ALCOHOL OF THE SERIES $C_nH_{2n-6}O$

FICOCERYL ALCOHOL,[2] $C_{17}H_{28}O$

Ficoceryl alcohol is said to form the alcoholic constituent of gondang wax; it melts at 198° C. The uneven number of carbon atoms would suggest the desirability of confirming the composition of this alcohol by a renewed investigation.

IV.—ALCOHOLS OF THE GLYCOLIC SERIES, $C_nH_{2n+2}O_2$

An alcohol of the composition  $C_{25}H_{52}O_2 = C_{23}H_{46}\left<\begin{matrix}CH_2.OH\\ CH_2.OH\end{matrix}\right.$ occurs, according to *Stürcke,*[3] in carnaüba wax as an ester. It is a crystalline powder, melting at 103·5°-103·8° C.; sparingly soluble in boiling petroleum ether, more readily soluble in ether and in benzene. On heating with soda-lime, a dibasic acid,  $C_{23}H_{46}\left<\begin{matrix}COOH\\ COOH\end{matrix}\right.$, is obtained.

COCCERYL ALCOHOL, $C_{30}H_{62}O_2$

Cocceryl alcohol occurs as cocceryl coccerate in the wax of cochineal (*Liebermann*). It is a crystalline powder (from alcohol) melting at 101°-104° C. By oxidation with chromic acid in acetic acid solution, pentadecylic acid, $C_{15}H_{30}O_2$, is obtained.

V.—ALCOHOLS OF THE SERIES $C_nH_{2n+2}O_3$

GLYCEROL, $C_3H_8O_3 = CH_2(OH).CH(OH).CH_2(OH)$

Glycerol[4] occurs in combination with fatty acids in all fatty oils and fats; it was discovered by *Scheele*[5] when preparing lead plaister from olive oil, and was termed by him "principium dulce." It is found in the free state in fermented alcoholic liquors,[1] and also in blood.[2] One hundred parts of sugar produce 3-5 parts of glycerol. The synthetical preparation of glycerol has only theoretical interest, and, therefore, falls outside the scope of this work.[3] The technical production of glycerol will be dealt with exhaustively in Vol. III. Chap. XV. under "Glycerin Manufacture."

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[1] *Journ. Soc. Chem. Ind.,* 1896, 15.

[2] Greshoff and Sack, *Rec. d. trav. chim. Pays-Bas,* 1901, 65.

[3] *Liebig's Annal.* 223, 283.

[4] *Glycerol* denotes here the chemical individual $C_3H_8O_3$, whereas the technically prepared chemically pure glycerin represents only the nearest approach to glycerol. All technical preparations are best termed "*glycerin,*" as is the case in commerce.

[5] *Crell's Chem. Annal.* 1783, 99.

Glycerol (purest, "chemically pure" glycerin) is a colourless,[4] odourless, viscid liquid, having a sweet taste. It is optically inactive and is neutral to indicators. On exposure to an intense cold for a prolonged time, it crystallises in rhombic crystals melting at 20° C. With the aid of a few crystals, large quantities of glycerol can easily be converted into a crystalline mass at 0° C.[5]

Glycerol is oily to the touch, and produces on the skin, especially on the mucous membranes, the sensation of heat, due to its absorbing moisture from the tissues. The water-absorbing power of glycerol is so great, that on exposure to the atmosphere as much as 50 per cent of its own weight of water is taken up. A formula for calculating the hygroscopic power of glycerin has been given by *A. Kailan*.[6]

The numbers recorded by several observers for the specific gravity of pure glycerin do not agree, owing, no doubt, to the difficulty of freeing it from the last traces of water, which can only be removed completely by allowing to stand *in vacuo* over sulphuric acid for some prolonged time.[7] The most reliable values are the following:—$d^{15°}_{15°}$ C. = 1·26468, $d^{17·5°}_{17·5°}$ C. = 1·2620. *Kailan*[6] gives the general formula for temperatures between 14·3° and 20·6° C.:—$d^{t}_{4} = 1·26143 + (15 - t) \times 0·000632$. Further information will be given in Chapter XV., where also the refractive indices at different temperatures will be found.

At the ordinary temperature glycerol does not volatilise; at the boiling point of water, however, appreciable quantities escape as vapour. Hence, if glycerol be heated in an open dish on a water-bath, a slight loss is incurred, such loss depending on the shape of the vessel (whether deep or shallow), the area of the surface exposed,[8] and the frequency with which the air over its surface is renewed.

Glycerol boils under 760 mm. pressure at 290° C. (cp. also table of Vapour Tensions, p. 246), with slight decomposition only. At pressures below 12 mm. it distils unchanged.

The following table contains the most reliable observations of boiling points under reduced pressures:[9]—

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[1] The recovery of glycerin from the residues of fermented liquors falls outside the scope of this work.

[2] Nicloux, *Compt. rend.*, 1903 (136), 764. Cp. Mouneyrat, *Bull. Soc. Chim.*, 1904 (31), 409. Cp. Levites, *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1908 (57), 47. Reach, *Biochem. Zeits.*, 1908 (xiv.), 279.

[3] Cp. also A. Catilion, *De la Glycérine.* Paris, 1903. C. Naud.

[4] Cp. W. Spring, *Journ. Chem. Soc.* Abstr. i. 119.

[5] Cp. Tammauri, *Zeits. f. angew. Chem.*, 1905, 15.

[6] *Zeits. f. anal. Chem.*, 1911 (51), 81.

[7] Clausnitzer, *Zeits. f. analyt. Chem.* 20, 65.

[8] Nessler and Barth, *Berichte*, 1884, 17, Ref. 543.

[9] Cp. also Richardson, *Journ. Chem. Soc.*, 1886, 746.

Pressure. mm.	Boiling Point. °C.
385·33	260·4
347·10	257·3
231·87	250·3
201·23	241·8
100·81	220·3
50·00	210·0
45·61	201·3
30·00	191·8
20·46	183·3
20	182[1]
15	176[1]
12·50	179·5
10·00	167·2
6·53	161·3
5·00	155·5
0·24	118·5[2]
0·056	115-116[3]

Glycerol is miscible with water in all proportions. On mixing water with glycerol a contraction of volume and an increase of temperature takes place. The greatest increase of temperature—viz. 5° C.—is observed when 58 parts of glycerol (by weight) are mixed with 42 parts of water; the greatest contraction equals 1·1 per cent (*Gerlach*).

The vapour pressure of a dilute solution of glycerol rises with the rise of temperature of the boiling solution, so that considerable amounts of glycerol volatilise with the water vapour. Theoretically, a mixture of saturated water and glycerol vapours, under the ordinary atmospheric pressure, cannot contain more than 0·2 to 0·3 per cent of glycerol, provided that the two vapours are not miscible. Since, however, glycerol and water are miscible in every proportion, the composition of the escaping vapours cannot be calculated according to Dalton's well-known law, but must be derived from actual observations. *Gerlach* determined, with the aid of a vaporimeter, in which the pressure of the vapour was measured by a column of mercury, the vapour pressures given in the following table:—

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[1] *Zeits. f. anal. Chem.*, 1911 (51), 81.

[2] E. Fischer and C. Harries, *Berichte*, 1902, 2158, give 143° C as the boiling point under 0·2 mm. pressure (temperature of the bath 180° C.).

[3] E. Erdmann, *Berichte*, 1903, 3461.

Vapour Tensions of Glycerol and of its Aqueous Solutions (*Gerlach*[1])

Glycerol.	Water.	Boiling Point at 760 mm. Pressure.	Vapour Pressure at 100° C.
Per cent.	Per cent.	° C.	
100	0	290	64
99	1	239	87
98	2	208	107
97	3	188	126
96	4	175	144
95	5	164	162
94	6	156	180
93	7	150	198
92	8	145	215
91	9	141	231
90	10	138	247
89	11	135	263
88	12	132·5	279
87	13	130·5	295
86	14	129	311
85	15	127·5	326
84	16	126	340
83	17	124·5	355
82	18	123	370
81	19	122	384
80	20	121	396
79	21	120	408
78	22	119	419
77	23	118·2	430
76	24	117·4	440
75	25	116·7	450
74	26	116	460
73	27	115·4	470
72	28	114·8	480
71	29	114·2	489
70	30	113·6	496
65	35	111·3	553
60	40	109	565
55	45	107·5	593
50	50	106	618
45	55	105	639
40	60	104	657
35	65	103·4	675
30	70	102·8	690
25	75	102·3	704
20	80	101·8	717
10	90	100·9	740
0	100	100	760

From the foregoing numbers an approximate estimate can be derived as to the losses that may be incurred on evaporating dilute solutions of glycerol.

Experiments showed that up to a concentration of about 50 per cent, no glycerol escapes with the water vapours, even if the dilute solutions be kept boiling for some prolonged time. At a concentration of about 70 per cent, traces of glycerol escape from the boiling solution (cp. *Hehner*[2]).

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[1] This table is reproduced as part of a table given in the 2nd edition of this work, 1898, p. 800.

[2] *Analyst*, 1887, 65.

The boiling point of such a solution is 113·6° (see table). Above this concentration, notable amounts of glycerol escape, so that the quantitative determination of glycerol in an aqueous solution by evaporating it down on the water-bath leads to faulty results. Even if the concentration of glycerol solutions be carried out *in vacuo*, considerable proportions of glycerol escape with the water vapours, when the concentration of the solution exceeds 80 per cent (*Lewkowitsch*).

Tables giving the specific gravities of dilute solutions will be found in Vol. III. Chapter XV. under " Glycerin Manufacture."

For the coëfficients of expansion of glycerol cp. Vol. III. " Glycerin Manufacture."

On electrolysing glycerol on platinum anodes *Renard*[1] and *M'Coy*[2] found that glycerol is decomposed into carbonmonoxide, carbondioxide, acetic acid, glyceraldehyde (glycerose) and an acid, probably glyceric acid. *W. Loeb*,[3] on electrolysing glycerol in a 5 per cent sulphuric acid solution on lead anodes found that formaldehyde is formed in considerable quantity. There was also formed a syrupy mass free from glycolaldehyde, glyceraldehyde, dioxyacetone, and hexose, but containing a pentose, very probably i-arabinose, and, as insoluble acids, tartronic and trioxyglutaric acids. The only volatile acid found was formic acid, most probably originating from formaldehyde.

By the action of *ultra-violet rays* on neutral glycerol at 25° C. in the presence of air, glyceraldehyde (glycerose) is formed. If the glycerin be rendered alkaline, β-acrose is obtained.[4]

The ordinary products of *fermentation* of glycerol are :—butyric, lactic, and succinic acids, glycerose, and dioxyacetone, none of which yield acroleïn. *E. Voisenet*,[5] however, has found a facultative aerobic bacillus producing the " bitterness " of wine, which gives rise to the formation of aldehyde. (Cp. also footnote 3, p. 251.)

Glycerol is miscible with alcohol in all proportions; it dissolves easily in a mixture of alcohol and ether, but is sparingly soluble in ether alone, one part of glycerin, specific gravity 1·23, requiring about 500 parts of ether. It is therefore impossible to extract glycerol from its aqueous solution by means of ether. Glycerol is soluble in acetone. (For the quantitative determination of glycerol by means of acetone see Chap. VI.). Nine parts of glycerol are soluble in 100 parts of ethylacetate. Glycerol is insoluble in chloroform, petroleum ether, carbon bisulphide, and benzene; it is also insoluble in oils and fats (*Lewkowitsch*).

On heating glycerol slowly in a platinum dish to 150°-160° C., it evaporates without leaving a residue; at 150° C. it will burn with a bluish, non-luminous flame without emitting odour.[6] If, however, glycerol is heated rapidly in a platinum dish, it burns with formation

[1] *Compt. rend.*, 1875 (81), 188; 1876 (82), 562.

[2] *Amer. Chem. Journ.*, 1893 (15), 656.

[3] *Zeits. f. Elektrochem.*, 1910 (16), 1.

[4] H. Bierry, V. Henri, and A. Ranc, *Compt. rend.*, 1911 (152), 535; 1912 (154), 1261.

[5] *Compt. rend.*, 1911 (153), 363.

[6] On this property rests the construction of *Schering's* "glycerin lamp."

of acroleïn, and yields a residue consisting of polyglycerols (cp. Vol. III. "Glycerin Manufacture").

The penetrating smell of *acroleïn* (which is also noticed when glycerides are burnt, *e.g.* when an oil lamp or a tallow candle has been blown out) serves as the most characteristic reaction for the detection of the smallest quantities of glycerol. For this purpose it is best to mix the substance under examination with dehydrating substances, such as hydrogen potassium sulphate[1] or phosphoric acid,[2] when acroleïn[3] is formed readily. The most delicate reagents for detecting acroleïn in aqueous solutions are:—an ammoniacal solution of silver nitrate (reduction to metallic silver with production of a mirror) and *Schiff's* reagent, a solution of rosaniline which has been decolourised by sulphur dioxide (restoration of the pink colour). The rosaniline test, however, is less delicate than the silver test.

If the quantity of glycerol under examination be very small, some uncertainty may arise owing to the evolution of sulphur dioxide, of vapours of sulphuric acid, and of empyreumatic substances. Hence it is best to isolate the acroleïn in the following manner (*Grünhut*):[4]—The substance is mixed in a flask with twice its weight of finely powdered potassium bisulphate. (*Senderens* showed that aluminium sulphate has the same accelerating action.) The flask is closed by a perforated cork fitted with a suitably bent tube, and heated in a sand-bath. The escaping gases are condensed in a test-tube immersed in a freezing mixture. In the presence of glycerol the condensate in the test-tube will smell distinctly of acroleïn. On adding to the contents of the test-tube a few drops of a reagent, prepared by dissolving 3 grms. of silver nitrate in a mixture of 30 grms. of ammonia of the specific gravity 0·923 and a solution of 30 grms. of caustic soda in 30 grms. of water, a silver mirror will be obtained if acroleïn be present.

This reagent should not be kept in stock, as the author[5] found that a bottle containing this reagent kept in the dark for about one week was shattered completely by an explosion. It is very likely that reduction of the nitrate to the explosive silver amide or nitride had taken place.

In view of the extreme delicacy of the acroleïn tests, colour reaction recommended by several authors, appear to be superfluous. The tests enumerated below are, therefore, only given for the sake of completeness.

Lewin[6] recommends to prepare a solution of piperidine in sodium nitro-prusside and add to the condensate containing acroleïn. In a dilution of 1 : 100 a gentian-blue colouration is obtained, and in a dilution of 1 : 1000 a pure blue. The blue colouration is still noticeable in a dilution of 1 : 2000.

The green colouration which a borax bead moistened with a dilute glycerol solution gives in the flame test, cannot be considered characteristic, as this is a general reaction of alcohols. If a glycerol solution be added to a cold solution of borax, made pink by addition of phenolphthalein, the colouration disappears. On heating, the pink colour reappears, to disappear again on cooling. This reaction cannot be used for the detection of small amounts of glycerol, as considerable quantities of glycerol are required to discharge the pink colour of a borax solution. The proposal has been made to estimate boric acid by means of glycerol (and *vice versa*), but this method cannot be recommended.[1] According to *Grün and Bockisch*,[2] no glyceryl borates, but complex salts of metaborates with glycerol (see below, " *Glycerinates* ") are formed.

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[1] Redtenbacher, *Liebig's Annal.*, 1843 (47), 113. Colour reaction, C. Denigès, *Compt. rend.*, 1909 (148), 570.

[2] *Journ. f. prakt. Chem.*, 1909, 322.

[3] Acroleïn, C_3H_4O, is a liquid of a most penetrating odour. Its vapours affect the eyes, causing a copious flow of tears. It is readily soluble in water, boils at 42·4° C., and is easily converted into a resinous mass on exposure to the air. With regard to the preparation of acroleïn cp. G. Fr. Bergh, *Journ. f. prakt. Chem.*, 1909 (79), 351; J. B. Senderens, *Compt. rend.*, 1910 (151), 530; A. Wohl and B. Mylo, *Berichte*, 1912, 2046.

[4] *Zeits. f. analyt. Chem.*, 1899, 41.

[5] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1912, 311.

[6] *Berichte*, 1899, 3388.

Glycerol has powerful solvent properties; it combines in this respect the properties of water and alcohol; many substances are more easily dissolved by it than by either water or alcohol. The following table of solubilities will serve to illustrate this :—

100 parts of glycerol dissolve at 15° C.	98	parts of crystal soda.
	60	,, ,, borax.
	50·5	,, ,, potassium arsenate.
	50	,, ,, sodium arsenate.
	50	,, ,, zinc chloride.
	48·8	,, ,, tannic acid.
	40	,, ,, alum.
	40	,, ,, zinc iodide.
	40	,, ,, potassium iodide.
	35·2	,, ,, zinc sulphate.
	32	,, ,, potassium cyanide.
	30	,, ,, copper sulphate.
	25	,, ,, ferrous sulphate.
	25	,, ,, potassium bromide.
	20	,, ,, lead acetate.
	20	,, ,, ammonium carbonate.
	20	,, ,, arsenious acid.
	20	,, ,, arsenic acid.
	20	,, ,, ammonium chloride.
	15	,, ,, oxalic acid.
	11	,, ,, boric acid.
	10	,, ,, barium chloride.
	10	,, ,, copper acetate.
	10	,, ,, benzoic acid.
	8	,, ,, sodium bicarbonate.
	7·5	,, ,, mercury bichloride.
	5	,, ,, calcium sulphide.
	3·7	,, ,, potassium chloride.
	3·5	,, ,, potassium chlorate.
	1·9	,, ,, iodine.
	about 1	part of calcium sulphate.
	,, 0·1	,, ,, sulphur.
	,, 0·25	,, ,, phosphorus.

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[1] Cp. A. Beythien and H. Hempel, *Zeits. f. Unters. d. Nahrgs-. u. Genussm.*, 1899, 842; Grünhut, *Zeits. f. analyt. Chem.*, 1899, 39; Hundeshagen, *Zeits. f. angew. Chem.*, 1901, 73; N. Tananajew and D. Zuckermann, *Journ. Russ. Phys. Chem. Soc.*, 1909 (41), 1469.

[2] *Berichte*, 1908, 3469.

An aqueous solution, of specific gravity 1·114, dissolves 0·957 per cent of calcium sulphate. Metallic soaps (which are insoluble in water) are to some extent dissolved: thus—

100 parts of glycerol, sp. gr. 1·114, dissolve	0·71 parts of iron oleate.
	0·94 ,, ,, magnesium oleate.
	1·18 ,, ,, calcium oleate.

On adding potassium permanganate to a solution of glycerol acidulated with sulphuric acid, decolouration takes place very slowly. Even on boiling, the glycerol is oxidised with difficulty. *Lenz* [1] showed that on boiling an acidulated solution of glycerol with an excess of a 1 per cent solution of potassium permanganate, no more than 34 per cent of the theoretical amount required for complete oxidation is reduced. Only by a large excess of concentrated permanganate solution can glycerol be oxidised to carbonic acid. *Campani and Bizzarri* [2] state that on oxidising glycerol with potassium permanganate in alkaline solution, the following products are obtained: carbonic, formic, acetic, propionic, and oxalic acids, and small quantities of tartronic acid. If, however, the oxidation in alkaline solution be carried out according to the directions given by *Benedikt and Zsigmondy* (see "Quantitative Estimation of Glycerol," Chap. VI.), glycerol is completely converted into oxalic and carbonic acids according to the following equation:—

$$C_3H_8O_3+2K_2Mn_2O_8=K_2C_2O_4+K_2CO_3+4MnO_2+4H_2O.$$

Complete oxidation to carbon dioxide and water also takes place when glycerol is oxidised with potassium bichromate and sulphuric acid. This is expressed by the following equation:—

$$3C_3H_8O_3+7Cr_2O_7K_2+28SO_4H_2=7[Cr_2(SO_4)_3+SO_4K_2]+9CO_2+40H_2O$$

or in a simpler form thus—

$$2C_3H_8O_3+7O_2=6CO_2+8H_2O.$$

Dry potassium permanganate reacts violently with concentrated glycerol. If finely powdered potassium permanganate be heaped up to form a small truncated cone, and concentrated glycerin be poured into a hole made on the top, fumes escape; after a very short time the glycerin commences to froth, and ignites spontaneously with violent evolution of gases.[3]

Hydrogen peroxide oxidises glycerol to formic acid, glyceric and glycolic acids being formed as intermediate products. Thus the final product of oxidation of one molecule of glycerin consists of one molecule of carbondioxide, two molecules of water, and two molecules of formic acid.[4]

By gentle oxidation with nitric acid glycerol yields glyceric and oxalic acids together with formic, glycolic, glycoloxylic, and racemic acids. The glyceric acid so obtained is a racemic compound which can be resolved into optically active, enantiomorphous glyceric acids (*Lewkowitsch* [1]).

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[1] *Journ. Soc. Chem. Ind.*, 1885, 368.

[2] *Gazz. chim. ital.*, 1884 (12), i.

[3] Dvorak, *Chem. Zeit.*, 1902, 903; cp. also Namias, *ibid.*, 1906, 64.

[4] J. Effront, *Bull. Soc. Chim. de France*, 1912 (11), 744.

A strong aqueous solution of glycerol reduces *Fehling's* solution only slightly. On boiling the solution for ten minutes, and allowing it to stand for twenty-four to forty-eight hours, a red or a yellow precipitate is obtained. If, however, the glycerol be diluted with ten times its bulk of water no reduction occurs.

A mixture of glycerol and silver nitrate solution heated at the temperature of boiling water, with a few drops of ammonia, gives a precipitate of metallic silver. If ammonia solution be added to glycerol in the cold, and heat be then applied, as a rule no reduction takes place on adding silver nitrate, simply because the glycerol has not been heated sufficiently; the addition of caustic soda or potash, however, causes metallic silver to separate slowly. According to *Bullnheimer* [2] 1 part of metallic silver corresponds to 11·3 parts of glycerol.

On heating glycerol with solid caustic soda, acrylic acid is formed (*Redtenbacher*), and finally formic and acetic acids (*Dumas and Stas*), as also "fermentation" [3] lactic acid. If an excess of caustic alkalis be used, formic and oxalic acids are obtained. According to *J. U. Nef*, glycerol, heated with one molecule of sodium hydroxide, yields propylene glycol; and treated with sodium hydroxide and mercuric oxide it yields glyceric acid On heating with small quantities of caustic potash —0·5 per cent—glycerol is condensed to polyglycerols (*Claessen* [4]).

Metallic Glyceroxides—Glycerates

Glycerol dissolves caustic alkalis, alkaline earths (*Chevreul*), and lead oxide to form chemical compounds. Lime, strontia, and baryta are precipitated nearly completely from such solutions by carbon dioxide, a small quantity only of the earths escaping precipitation. In presence of caustic alkalis, glycerol also dissolves ferric oxide,[5] cupric oxide, and bismuth oxide, no doubt owing to the formation of soluble compounds (*metallic glyceroxides*) such as are represented by monosodium-cupro-glyceroxide (see below). The above oxides are not reduced to metal, or at most only to the lower oxides. However, the following oxides: silver oxide (cp. above), gold oxide, mercury oxide, rhodium oxide, palladium oxide, and platinum oxide (Ag_2O,

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[1] *Berichte*, 1883, 2720.

[2] *Forschungsberichte über Lebensmittel, etc.*, 4, pp. 12, 31.

[3] On allowing glycerol to ferment by means of *Bacillus butylicus* in presence of calcium carbonate and nutritive salts E. Buchner and Meisenheimer (*Berichte*, 1908, 1410) obtained normal butylic alcohol, ethyl alcohol, and (as by-products) normal butyric acid, acetic acid, formic acid, lactic acid, carbon dioxide, and hydrogen. With regard to the formation of glycerol by fermentation cp. W. Seifert and R. Reisch, *Zentralbl. f. Bakteriologie*, 1904 (ii), 12, 574. Reisch, *Zentralbl. f. Bakter.*, 1907 (ii), 18, 396 (cp. also above, p. 247).

[4] German patent 198,768.

[5] Cp. Puls, *Journ. f. prakt. Chem.*, 1877 (15), 83; Denigès, *Ann. chim. analyt.*, 1898, 229. With regard to colloidal compounds of ferric hydrate, glycerol, and caustic potash, cp. Grimaux, *Bull. Soc. Chim.* 42, 207; *Compt. rend.*, 1884 (98), 1434; 1485.

Au_2O_3, HgO, RhO_2, PdO, PtO_2), are reduced to metals when heated with alkaline glycerol solution (*Bullnheimer* [1]).

Freshly precipitated cero-hydroxide is very easily soluble in glycerol; this solution is readily dissociated by addition of water. The solution becomes turbid very gradually, and finally the hydroxide is precipitated in a gelatinous form (*A. Müller* [2]). Turbidity of the perfectly clear solution sets in the more rapidly, the more dilute the original solution was.

The following glyceroxides have been prepared in a pure state :—

Monosodium glyceroxide, $NaC_3H_7O_3$, obtained by mixing a solution of metallic sodium in absolute alcohol (*i.e.* sodium ethoxide) with glycerol. A precipitate is formed consisting of extremely deliquescent, rhombic crystals having the formula $NaC_3H_7O_3 + C_2H_6O$. On heating to 100° C., the molecule of alcohol escapes, leaving behind the monosodium glyceroxide as a white, highly hygroscopic powder, which is converted by water into glycerol and caustic soda. If, in the preparation of monosodium glyceroxide, sodium methoxide be used, the crystalline compound has the composition: $NaC_3H_7O_3 + CH_4O$. According to *J. U. Nef*, sodium glyceroxide is an α-derivative, $CH_2(OH).CH(OH).CH_2.ONa$.

The product obtained by the action of metallic sodium on glycerin has led to the commercial preparation of a solid substance—" gazeline pralinée "—for the production of hydrogen for military purposes. A portable gas-producer based on this principle was introduced in 1879, but notwithstanding many improvements by *Renard*, the process was abandoned. In view of the modern processes for producing hydrogen this method is only of historical interest.

Disodium glyceroxide, $Na_2C_3H_6O_3$, is prepared by triturating the crystals of monosodium glyceroxide, under absolute alcohol, with one molecule of sodium ethoxide, and boiling the mixture for several hours.

With regard to the trisodium compound cp. Chap. II. p. 103.

The potassium derivatives closely simulate the sodium compounds.

Calcium glyceroxide, $CaC_3H_6O_3$, is a crystalline powder obtained by heating 14 parts of calcium oxide with 23 parts of anhydrous glycerol to 100° C., and cooling the mixture as soon as a violent reaction sets in. Water decomposes it into calcium oxide and glycerol (*Destrem* [3]).

Barium glyceroxide, $BaC_3H_6O_3$, is a deliquescent powder. It is prepared by warming 67·1 parts of anhydrous glycerol with 100 parts of baryta to 70° C. Hot water decomposes it rapidly into glycerol and baryta; cold water acts but slowly on it (*Destrem* [3]).

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[1] *Forschungsber. über Lebensmittel, etc.* 4, pp. 12, 31; cp. also A. Müller, *Zeits. f. anorg. Chem.*, 1905 (43), 321.

[2] *Zeits. f. anorgan. Chemie*, 1905 (43), 310. Biltz (*Nachrichten d. Königl. Ges. d. Wissensch., Göttingen*, 1906, Heft 2, p. 1) showed by observing this phenomenon under the ultra-microscope, that the separation of the hydroxide takes place in a continuous manner; at first very few single particles are noticeable; they then increase somewhat rapidly, and finally a colloidal precipitate is formed (cp. Vol. III. Chap XV. "Soap Manufacture").

[3] *Ann. de Chim. et de Phys.* [5], 27, 20; cp. also Grün and Husmann, *Berichte*, 1910, 1291, and J. Husmann, *Inaug. Dissert.*, Zürich, 1909, who consider these compounds as glycerinates and therefore ascribe to them formulæ exemplified by $C_3H_5(OH)_3Ba(OH)_2$.

Monoplumbo-glyceroxide, $PbC_3H_6O_3$, is prepared by adding 500 grms. of lead hydroxide (obtained by pouring a warm solution of lead nitrate into a large excess of warm ammonia and drying the precipitate on the water-bath) to 1000 grms. of boiling glycerin (85 per cent) with constant stirring. The mass is then cooled to 0° C., and 2500 c.c. of alcohol are added at 0° C.[1] The monoplumbo-glyceroxide thus prepared contains nitric acid, and has probably the composition $2Pb.C_3H_6O_3$, $Pb(NO_3)_2 + (OH)Pb(NO_3)$. A product free from nitric acid is obtained by *Morawski's*[2] method as follows:—Dissolve 22 grms. of lead acetate in 250 c.c. of water, add 20 grms. of glycerin, heat, and pour into the boiling solution a concentrated solution of 15 grms. of potassium hydrate. A slight precipitate is filtered off, and the filtrate is allowed to crystallise; in the course of a couple of days a large quantity of fine white needles, monoplumbo-glyceroxide, separate out.

If basic lead acetate be used instead of sugar of lead, basic plumbo-glyceroxides, of the composition $Pb_3(C_3H_5O_3)_2$ and $4PbC_3H_6O_3.PbO$, are obtained.

Disodium-mangano-glyceroxide, $Na_2(C_3H_5O_3)_2Mn$, is prepared by boiling anhydrous glycerol with a mixture of 1·1 parts of caustic soda solution, specific gravity 1·38, and 4 parts of freshly precipitated hydrated manganese peroxide.

Monosodium-cupro-glyceroxide[3] is prepared by heating 5 grms. of cupric hydrate, $Cu(OH)_2$, 15 c.c. of water, 2·5-3 grms. of glycerol, and 3 grms. of solid caustic soda in a flask until the caustic soda is dissolved, then adding 50 c.c. of 96 per cent alcohol, filtering off, and again adding alcohol until a distinct turbidity is noticed. Fine blue needles, having the composition $(NaCuC_3H_5O_3)_2 + C_2H_5OH + 9H_2O$, separate after six to ten hours' standing. On drying the crystals *in vacuo* at 100° C., the alcohol and 3 molecules of water are given off, leaving behind $(NaCuC_3H_5O_3)_2 + 6H_2O$. If copper nitrate be employed, hexagonal plates of the composition $(NaCuC_3H_5O_3)_2 + 3H_2O$ are obtained; these crystals are only formed in presence of a certain quantity of sodium nitrate.[4]

Monolithium-cupro-glyceroxide,[3] $LiCuC_3H_5O_3 + 6H_2O$, forms blue hexagonal plates.

Metallic Glycerinates

The great solubility in glycerol of zinc sulphate, also of nickel, cobalt, and copper sulphates, is explained by the fact that these salts combine with 3 molecules of glycerol to form complex compounds of the general formula $(M.3C_3H_8O_3)SO_4.H_2O$. For these compounds *Grün and Bockisch*[5] propose the name *glycerinates*, to distinguish them from the metallic glycerides (*glyceroxides*) described above. The glycerinates are precipitated from their aqueous solutions by alcohol as amorphous substances. The following glycerinates have been isolated in well-crystallised forms:[1] $[Ca.3C_3H_5(OH)_3]Cl_2$; $Ca(NO_3)_2 + 4C_3H_5(OH)_3$. For the existence of a *potassium cupriglycerate*, cp. *S. U. Pickering.*[2]

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[1] Fischer and Tafel, *Berichte*, 1888, 2635.

[2] *Journ. f. prakt. Chem.* [2], 22, 406.

[3] Bullnheimer, *Berichte*, 1898, 1453; 1899, 2347; Bullnheimer and Seitz, *ibid.*, 1900, 817.

[4] For the oxygen-absorbing properties of the potassium-cupro-compound (which has, however, not been isolated) and the oxidation products formed, cp. W. Traube, *Berichte*, 1910, 764.

[5] *Berichte*, 1908, 3465; cp. also Grün and Boedecker, *ibid.*, 1910, 1055.

Esters of Glycerol

The most important esters of glycerol are those resulting from the combination of glycerol with fatty acids.

It has been shown above (Chap. I.) that the natural oils and fats are the tri-acid esters (triglycerides, simple or mixed) of the fatty acids enumerated in the first part of this chapter. The tri-acid esters which have been obtained hitherto in a pure state—from tri-formin upwards—have been described in Chapter I. The natural oils and fats which in the present state of our knowledge must be regarded as a mixture of a number of simple and mixed triglycerides will be exhaustively described in the second volume of this work.

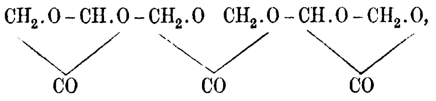
It has also been pointed out that glycerol is able to form mono-acid and di-acid esters. These are usually described as monoglycerides and diglycerides, although these terms must be considered incorrect; for the term monoglyceride would more appropriately apply to a triglyceride containing one and the same acid radicle, and the term diglyceride to a triglyceride containing two different acid radicles. The mono- and di-glycerides hitherto synthetically prepared have been described in Chapter I. It has been stated already that mono- and di-glycerides do not occur in nature.

Glycerol also forms esters with inorganic acids. In the following lines are described esters of carbonic, sulphuric, nitric, phosphoric, boric, and arsenious acids, some of which have acquired great importance in the arts and in pharmacy.

A mixed triglyceride containing two acid radicles of *fatty acids* and one of *phosphoric* acid occurs in nature; it has been described above as *lecithin* (p. 39).

CARBONIC ESTERS.—Glyceryl esters of carbonic acid are formed by heating glycerin with phenylcarbonate or with phosgene.[3]

The *tri-ester,*



$$\begin{array}{c}
CH_2.O-CH.O-CH_2.O\quad CH_2.O-CH.O-CH_2.O, \\
\diagdown\diagup\qquad\quad\diagdown\diagup\qquad\quad\diagdown\diagup \\
CO\qquad\qquad\quad CO\qquad\qquad\quad CO
\end{array}$$

is stated to be obtained by dissolving 10 parts of glycerin in 20 parts of pyridine and 80 parts of acetone, and passing 12 parts of phosgene through the solution.

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[1] Grün and Husmann, *Berichte*, 1910, 1291. Cp. J. Husmann, *Inaug. Dissert.*, Zürich, 1909; cp. also footnote 3, p. 252.

[2] *Journ. Chem. Soc.*, 1912, 185.

[3] Chemische Fabrik, Dr. R. Scheuble and Dr. A. Hochstetter, English patent 19,924, 1911, German patent 252,758.

The ester is obtainable in commerce under the name " Tricarbin " " Glycarbin," and forms a white powder melting at 149° C., insoluble in water and alcohol.

SULPHURIC ESTERS.—Glycerol dissolves easily in concentrated sulphuric acid to form esters; theory would predict that all three possible esters are formed. On boiling with steam they are readily dissociated into glycerol and sulphuric acid.

Glycerolmonosulphuric acid, $CH_2(O.SO_3H).CH(OH).CH_2(OH)$, was obtained by *Pelouze*[1] by dissolving 1 part of glycerol in 2 parts of sulphuric acid. This ester is said to be employed in the leather industry for " swelling " hides.[2] The free acid is very unstable. The calcium salt, $Ca[C_3H_5(OSO_3)(OH)(OH)]_2$, crystallises in needles;[3] it is readily decomposed by boiling with lime water. The distearo ester $CH_2.(O.SO_3H)CH(O.C_{18}H_{35}O).CH_2(O.C_{18}H_{35}O)$ and its brucine salt have been prepared by *Grün and Corelli*.[4]

Glyceroldisulphuric acid, $C_3H_5(OH)(O.SO_3H)_2$, is formed on treating glyceroltrisulphuric acid (see below) with hot water (*Claesson*[5]). The disulphuric acid is characterised by its barium-, and potassium salts.[6] *Grün*[7] stated that on treating glycerol with sulphuric acid the reaction does not proceed beyond the formation of glyceroldisulphuric acid, $C_3H_5(OH)(OSO_3H)_2$, even if a considerable excess of concentrated sulphuric acid be used. (This is in contradiction to the theoretical postulate.) *B. W. van Eldik Thieme*[8] has, however, been able to show that this statement is incorrect, for on dissolving 1 part of glycerol in 4 parts of 98·3 per cent sulphuric acid he obtained as chief products: glyceroldisulphuric and glyceroltrisulphuric acids, whilst a small proportion of glycerol monosulphuric acid could also be identified.

Glyceroltrisulphuric acid, $CH_2(O.SO_3H).CH(O.SO_3H).CH_2(O.SO_3H)$, prepared by the action of chlorosulphonic acid, $SO_2(OH)Cl$, on glycerol at 0° C. (*Claesson*[9]), forms hygroscopic crystals. *Claesson's* statement that the ester is readily hydrolysed by boiling with water, is controverted by *van Eldik Thieme*,[10] who has shown that a solution of 21·5 grms. of the ester dissolved in 500 c.c. of water required no less than eighteen hours' boiling for complete hydrolysis.

PHOSPHORIC ESTERS, GLYCERYLPHOSPHORIC (GLYCEROPHOSPHORIC) ACIDS.—A mixed fatty acid-phosphoric glyceryl-ester has been described above as lecithin. The esters have recently acquired considerable commercial importance in pharmaceutical practice on account of their being used (in the most varied forms) as nerve stimulants. Their relationship to *lecithin* has undoubtedly contributed to the preparations which have come somewhat into vogue.[1]

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[1] *Liebig's Annal.* 19, 211.

[2] German patent 86,334 (Schmelzer and Aschmann).

[3] *Liebig's Annal.* 20, 48.

[4] *Zeits. f. ang. Chem.*, 1912, 669.

[5] *Journ. f. prakt. Chem.* [2], 20, 6.

[6] Grün and Schacht, *Berichte*, 1907, 1780. Custodis, *Inaug. Dissert.*, Zürich, 1909.

[7] *Berichte*, 1905, 2284.

[8] *Proceed. K. Akad. v. Wetensch.*, Amsterdam, 1908, 855. *Journ. f. prakt. Chem.*, 1912 (85), 296.

[9] *Journ. f. prakt. Chem.* [2], 20, 4.

[10] *Ibid.*, 1912 (85), 306.

Glyceromonophosphoric acid, $CH_2(OH).CH(OH).CH_2.OPO.(OH)_2$, first obtained by *Pelouze*,[2] is prepared by heating 3 parts of a 60 per cent solution of phosphoric acid with 3·6 parts of glycerol for 6 days at 105° C. (*Portes and Prunier* [3]). The free acid cannot be obtained by decomposing with a mineral acid its potassium or barium salts, as phosphoric acid is split off (*Adrian and Trillat* [2]). The artificially prepared glycerophosphoric acid is most likely a racemic compound, inasmuch as the glycerophosphoric acid obtained from lecithin was found to be optically active (see p. 38).

On neutralising with standard alkali the acid behaves like a *dibasic* acid to phenolphthalein, and like a monobasic acid to methylorange.

The *calcium* salt, $Ca[C_3H_5(OH)_2(OPO_3)]_2+2H_2O$, crystallises in scales; it is soluble in 15 parts of cold water, nearly insoluble in boiling water and alcohol. Boiling with water does not decompose the salt; hence the commercial product can be freed from glycerol and from phosphoric acid by boiling water.[4] The *barium* salt is readily soluble in water; the aqueous solution is readily decomposed on boiling.

Glycerodiphosphoric acid, $PO[O.C_3H_5(OH)_2]_2OH$, is obtained by prolonged heating of phosphoric acid with glycerol (*Adrian and Trillat* [5]).

On heating with water or alcohol phosphoric acid and glycerolmonophosphoric acids are formed; alkali carbonates effect this resolution in the cold.

Glycol and glycolhydrine esters of this acid have been prepared by *Grün and Kade*.

Glycerotriphosphoric ester (*Carré* [6]) is formed by heating glycerol with the equivalent amount of phosphoric acid *in vacuo* for 10 to 12 hours to 130° C. By adding 1 molecule of glycerol to this ester a less stable di-ester (diglycerotriphosphoric acid) is formed (*A. Contardi* [7]). This statement is, however, contested by *Carré*.[8]

The salts of glycerophosphoric acids — glycerophosphates[9] of sodium, lithium, calcium, strontium, iron, etc.—are now largely used in pharmaceutical practice, especially in France. These not infrequently contain gross impurities.

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[1] For an artificial "lecithin" cp. German patent 193,189 (Ulzer and Batik). For the velocity of hydrolysis of glycerophosphoric acids cp. F. Malengreau and G. Prigent, *Zeits. f. physiol. Chem.*, 1911 (73), 68.

[2] *Compt. rend.*, 1898 (126), 215.

[3] *Bull. Soc. Chim.* [3], 13, 96.

[4] The mixed salt of ammonia and calcium glycero-phosphates is patented by Darrasse Frères and L. Dupont in French patent 447,776.

[5] *Bull. Soc. Chem.* [3], 19, 269.

[6] *Compt. rend.*, 1903 (137), 1070; 1904 (138), 47; cp. also Imbert and Belugou, *Bull. Soc. Chim.*, 1900 (21), 935.

[7] *Gazz. chim. ital.*, 1912 (42), 270.

[8] *Compt. rend.*, 1912 (155), 1520.

[9] Cp. French patent 376,564, Poulenc Frères; German patent 208,700; P. Carré, *Bull. Soc. Chim. France*, 1909, 109; 1912, 169; A. Wülfing, German patent 217,553; Southall Bros. and Barclay, Ltd., and C. S. Roy, English patents 2806 and 2882, 1912; Southall Bros. and Barclay, Ltd., and E. W. Mann, English patent 2883, 1912; L. C. Reese, German patent 251,803; V. Paolini, *Gazz. chim. ital.*, 1912 (42), 57; *Chem. Fabrik auf Aktien, vorm.*, E. Schering, German patent 242,422, English patent 19,319, 1911; Rogier and Fiore, *Bullet. Sc. Pharmacolog.*, 1913, 7, 72.

GLYCEROPHOSPHITES were prepared by *A. Lumière, L. Lumière, and F. Perrin.*[1]

BORIC ESTER.—*Glyceryl borate,* $(C_3H_5O_3)B$, obtained by heating glycerol with boric anhydride (*Schiff and Bechi*[2]), forms a yellowish, very hygroscopic, glass-like mass. It is easily decomposed by water, but not by alcohol, even on boiling.

"*Boroform*" is termed a substance obtained by heating glycerol and borax, when in the first stage a glass-like, very viscous mass is formed to which the formula $[(C_3H_5)_4(H_2BO_3)_2(HNaBO_3)_2(OH)_5O_2]_2CH_2$ is ascribed.[3]

NITRIC ESTERS.—*Glyceryl mononitrate,* $CH_2(OH)CH(OH)CH_2.O.NO_2$, is obtained by mixing glycerol with a 25 per cent nitric acid (*Hanriot*[4]).

Will obtained the monoester as a by-product in the preparation of glycerol dinitrate. The mononitrate could be separated into two isomerides, one of which, crystallising at 58°-59° C., is described as α-mononitrate, yielding on nitration both isomeric dinitrates (see below), as also trinitrate. For further information see the table given below.

Glyceryl dinitrate, $C_3H_5(ONO_2)_2(OH)$, is obtained by running one part of glycerol drop by drop into 5 parts of a mixture consisting of 3 parts of concentrated sulphuric acid and 1 part of nitric acid, 9 parts of water being present for every 100 parts of total acids. Simultaneously, trinitroglycerin is formed (*Will*[5]). *Mikolajczek*[6] prepares the dinitrate by adding 33 parts of nitric acid, specific gravity 1·5, to 10 parts of glycerin with continuous stirring and cooling. *Will* considers it preferable to add the glycerin to the nitric acid. Dinitroglycerin dissolves in all proportions in dilute sulphuric acid and nitric acid ; it also dissolves in ether, alcohol, chloroform, acetone, and a little less readily in benzene than does trinitroglycerin. It is insoluble in carbon tetrachloride and in petroleum spirit. In its anhydrous state it gelatinises nitrocellulose very readily. Dinitroglycerin is more soluble in water than is trinitroglycerin ; a saturated solution at 15° C. contains 8 per cent of dinitrate.[7] Glyceryl dinitrate is as poisonous as the trinitrate.

Glyceryl dinitrate is dissociated by a 70 per cent sulphuric acid to mononitrate and glycerol. *Will* showed that the dinitrate exists in two modifications, he having been able to resolve crude dinitroglycerol into a crystalline compound "*Dinitroglycerol K,*" and an oily compound "*Dinitroglycerol F.*" (For further details see the table given below.)

Glyceryl trinitrate, Nitroglycerin, $C_3H_5(O.NO_2)_3$, is prepared by allowing glycerol to run into a mixture of 1 part of strongest nitric acid and 2 parts (by weight) of concentrated sulphuric acid. It is a heavy oily liquid of specific gravity 1·600 which volatilises at 160° C.

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[1] *Compt. rend.,* 1901 (133), 643.

[2] *Zeits. f. Chem.,* 1866, 147, cp. also Councler, *Journ. f. prakt. Chem.,* (2), 18, 380.

[3] *Chem. Zentralbl.,* 1911 (ii.), 99.

[4] *Ann. de Chim. et de Phys.,* 1905 [5], 17, 118, 365 ; *Compt rend.,* 1912 (154), 220.

[5] German patent 181,385 ; cp. also *Berichte,* 1908, 1107, and German patents 58,957 (Wohl), 205,752 (C. Pütz) ; English patent 6314, 1906 (A. Nobel & Co.).

[6] French patent 431,911.

[7] For the recovery of the dissolved dinitroglycerin cp. German patent 210,558, Castroper Sicherheitssprengstoff-Akt. Ges., Dortmund.

under a pressure of 15 mm.[1] Its most remarkable property is that of exploding violently under certain conditions. Nitroglycerin is manufactured on an extensive scale, and forms the main outlet for the bulk of the glycerin produced commercially (see Vol. III. Chap. XV.). It forms the chief ingredient of almost all modern "high explosives" and "smokeless powders." Thus "dynamite" is produced by mixing nitroglycerin with kieselguhr, whilst "blasting gelatin" is obtained by dissolving nitrocellulose in nitroglycerin. Nitroglycerin is also used in therapeutics, small doses being sufficient to dilate the blood-vessels.[2]

Nitroglycerin exists in two modifications: one is labile, melts at 2·8°-2·9° C., and solidifies at 2·0°-2·2° C.; the second occurs in a stable form, melting at 13·1°-13·2° C., and solidifying at 12·5° C. (*Kast*[3]).

Glyceryl trinitrate is hydrolysed by a 70 per cent sulphuric acid to glyceryl dinitrate and nitric acid.[4]

Having regard to the technical importance of the nitric esters, the following table, embodying *Wills'* results, will be found useful:—

	Mononitrate.	Dinitrate.	Trinitrate.
Specific gravity (at 15° C.) .	1·40	1·47	1·60
Melting point . . .	α-nitrate: 58° C. β-nitrate: 54° C.	α-nitrate: 26° C. β-nitrate: liquid.	Labile mod.: 2·2° C.[5] Stable mod.: 12·2° C.
Boiling point (at 15 mm.[6]) .	Both isomerides: 155-160° C.	Both isomerides: about 145° C.	Driven off at 160° C.[7] without boiling.
Solubility in water at 15° C.	70 per cent.	7·7 per cent.	0·16 per cent.
Hammer test (2 kgrms.) . Fall in cm.	..	Anhydrous: 7-10 cm. Crystalline: 30 cm.	Less than 4 cm.
Heat of explosion . .	..	Anhydrous: 1250 cal.	1600 cal.
Temperature of combustion	α-nitrate: 2812 cal.	K-anhydrous: 2088 cal. K-crystalline: 1986 cal. F: 2055 cal.	1570 cal.
Gelatinising properties .	..	Good.	Good.
Absorption of moisture .	50 per cent.	11 per cent.	0·2 per cent.

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[1] Lobry de Bruyn, *Rec. d. travaux chim. d. Pays-Bas*, 14, 133.

[2] *Journ. Soc. Chem. Ind.*, 1910, 387.

[3] *Zeits. f. d. ges. Schiess.- u. Sprengstoffwesen*, 1906 (i.).

[4] For the decomposition of trinitroglycerin by caustic akalis cp. Hay, *Moniteur scient.*, 1885 (27), 424; G. W. Macdonald, *Arms and Explosives*, 1908; E. Berl and M. Delpy, *Berichte*, 1910, 142. For the velocity of decomposition by heat see R. Robertson, *Journ. Chem. Soc.*, 1909, 1241.

[5] By recrystallising nitroglycerin repeatedly, S. Nauckhoff (*Zeits. f. d. ges. Schiess.- u. Sprengstoffwesen*, 1911 (6), 124) obtained only one modification, melting and solidifying at 13·3° C., whilst the labile modification could not be isolated.

[6] Cp. also A. L. Hyde, *Eighth Int. Congr. Appl. Chem.*, 1912, Sect. III. b. (4), 59.

[7] According to A. Marshall the vapour pressure is at 70° C. 0·051 mm. and at 18° C. – 0·001 mm. (calculated), *Journ. Chem. Soc.*, 1906 (89), 1371.

The mixed nitric esters, nitrodimethylester $CH_2(OCH_3)CH.O.NO_2.CH_2.O.CH_3$, and nitrodiethylester $CH_2.OC_2H_5.CH.O.NO_2.CH_2.O.C_2H_5$, have been prepared by *Paterno and Benelli.*[1]

Glyceryl arsenite, $C_3H_5AsO_3$, formed by dissolving 1 molecule of arsenious oxide in 2 molecules of glycerol and heating to 250° C. (*Jackson*), is a butter-like substance, melting at 50° C. to a thick liquid. It decomposes above 250° C., but is volatile with the vapours of glycerol. It has not yet been ascertained whether, on distillation in a current of superheated steam, the arsenite is volatilised unchanged, or is hydrolysed by the steam; at any rate, arsenious acid is found in the distillate.[2] Glyceryl arsenite is used in calico-printing.

In view of the importance the chlorohydrins and bromohydrins have acquired in the synthesis of mixed glycerides, and having regard to the considerable number of derivatives containing one or two fatty acid radicles, the preparation of the hydrins and their derivatives will be given here briefly.

Chlorohydrins

α-Monochlorohydrin, $CH_2Cl.CH(OH).CH_2(OH)$, obtained by heating glycerol with hydrochloric acid to 100° C. (*Berthelot*,[3] *Hanriot*[4]),[5] boils under 18 mm. pressure at 139° C.; $d^\circ = 1{\cdot}338$. It is miscible, in every proportion, with water, alcohol, and ether.

Esters of α-Monochlorohydrin

γ-Lauro-α-chlorohydrin, $C_3H_5(Cl).(OH).(O.C_{12}H_{23}O)$, obtained[6] from α-chlorohydrin and lauryl chloride, is a yellow oil, crystallising at −10° C. from petroleum ether in fine needles.

β-γ-Dilauro-α-chlorohydrin,[7] $C_3H_5(Cl)(O.C_{12}H_{23}O)_2$, is obtained by warming α-chloro-glyceroldisulphuric acid with lauric acid to 70° C. for 7½ hours. It crystallises from an alcohol-ether solution in microscopic needles, melting at 24° C.

γ-Myristo-α-chlorohydrin, $C_3H_5(Cl)(OH)(O.C_{14}H_{27}O)$,[8] obtained by heating myristyl chloride with an excess of 20-25 per cent of α-monochlorohydrin, is a yellowish mobile liquid, easily soluble in ether, petroleum ether, benzene, and somewhat sparingly soluble in cold alcohol.

β-γ-Dimyristo-α-chlorohydrin,[9] $C_3H_5(Cl)(O.C_{14}H_{27}O)_2$, is obtained either from α-chloro-glyceroldisulphuric acid, by the process described under α-chloro-distearin, or by warming α-β-dimyristin with thionyl-chloride on the water-bath, and crystallising the product from petroleum ether. The crystals prepared by the former process melt at 27°-29° C., those obtained by the latter process at 29° C. *Grün and Schreyer*[1] found the melting point 36° C.

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[1] *Gazz. chim. ital.*, 1909 (39), 312; cp. also V. Vender, German patent 209,943.

[2] Lewkowitsch, *Year-Book of Pharmacy*, 1890, 380.

[3] *Liebig's Annal.*, 1853 (88), 311.

[4] *Journ. f. prakt. Chem.* 18, 207.

[5] Cp. also German patents 197,308, 197,309, 201,230, 229,536, 238,341, 254,709; English patent 26,036, 1911; Sprengstoffwerke, Dr. R. Nahnsen & Co., French patent 437,315; United States patent 1,040,323; German patent 254,709.

[6] Grün and Skopnik, *Berichte*, 1909, 3751.

[7] Grün and Theimer, *Berichte*, 1907, 1799.

[8] A. Grün and B. Schreyer, *Berichte*, 1912, 3423.

[9] Grün and Theimer, *Berichte*, 1907, 1797.

γ-Palmito-α-chlorohydrin, $C_3H_5.(Cl)(OH)(O.C_{16}H_{31}O)$.[2]

β-γ-Dipalmito-α-chlorohydrin, $C_3H_5(Cl)(O.C_{16}H_{31}O)_2$, melts at 48°-50° C. (*Grün*;[3] *Corelli*[4]).

γ-Stearo-α-chlorohydrin, $C_3H_5.(Cl).(OH)(O.C_{18}H_{35}O)$, prepared from stearyl chloride and α-chlorohydrin, crystallises in white granular crystals (from a cooled mixture of ether and petroleum ether) melting at 48°-49° C.; the solidified mass melts at 39°-40° C.[5]

β-Stearo-α-chlorohydrin,[6] $C_3H_5(Cl)(O.C_{18}H_{35}O)(OH)$ is found amongst the products of hydrolysis, by means of concentrated (98 per cent) sulphuric acid, of β-γ-distearo-α-chlorohydrin.

γ-Myristo-β-stearo-α-chlorohydrin, $C_3H_5(Cl)(O.C_{18}H_{35}O)(O.C_{14}H_{27}O)$ (*Grün and Schreyer*[7]), obtained from γ-myristo-α-chlorohydrin and stearyl chloride, melts at 31° C.

γ-Stearo-β-myristo-α-chlorohydrin, $C_3H_5(Cl)(O.C_{14}H_{27}O)(O.C_{18}H_{35}O)$ melts at 26° C.

β-γ-Distearo-α-chlorohydrin,[8] $C_3H_5(Cl)(O.C_{18}H_{35}O)_2$, is prepared by heating α-chloro-glyceroldisulphuric acid, $C_3H_5(Cl)(SO_3H)(SO_3H)$, with stearic acid previously dissolved in concentrated sulphuric acid, to 70° C. for 3 hours. It crystallises from ether in white granules, easily soluble in chloroform and ether, sparingly soluble in petroleum ether and alcohol. The crystals melt at 56° C., and after solidification, at 41° C. The chlorine can only be replaced with difficulty by a hydroxyl group; the most suitable method consists in treating the chloro-compound with silver nitrite when the nitrite ester of the asymmetric distearin is formed. This ester is readily converted into β-distearin. On hydrolysing this chloro-distearin with concentrated sulphuric acid, products representing the several stages in the progress of hydrolysis could be isolated (see Chap. II. p. 76).

β-Monochlorohydrin, $CH_2OH.CHCl.CH_2OH$, is formed in small quantity when preparing α-monochlorohydrin, and is separated therefrom by fractionation *in vacuo*.[9]

Esters of β-Monochlorohydrin

α-Palmito-β-chlorohydrin, $C_3H_5(O.C_{16}H_{31}O).(Cl).(OH)$ (*Reinhardt*).

α-Stearo-β-chlorohydrin, $C_3H_5(O.C_{18}H_{35}O)(Cl)(OH)$ (*Reinhardt*).

α-γ-Dichlorohydrin, $CH_2Cl.CH.(OH).CH_2Cl$, obtained from glycerol and hydrochloric acid (*Berthelot*[10]), or from glycerol and sulphur chloride

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[1] *Berichte*, 1912, 3422.

[2] *Inaug. Dissert.*, Zürich, 1909.

[3] *Berichte*, 1905, 228.

[4] *Inaug. Dissert.*, Zürich, 1909.

[5] Grün and Skopnik, *Berichte*, 1909, 3751.

[6] *Berichte*, 1907, 1792.

[7] *Berichte*, 1912, 3425.

[8] Grün and Theimer, *Berichte*, 1907, 1793; 1800.

[9] Hanriot, *Ann. de Chim. et de Phys.* [5], 17, 73.

[10] *Liebig's Annal.* 92, 302.

(*Carius*,[1] *Claus*[2]), boils under ordinary pressure at 176°-177° C.; $d^{16} = 1{\cdot}396$. By heating dichlorohydrin with inorganic sulphides *Lilienfeld*[3] obtained solid, caoutchouc-like bodies.

Esters of α-γ-Dichlorohydrin

β-Aceto-α-γ-dichlorohydrin, $CH_2.Cl.CH(O.C_2H_3O).CH_2.Cl$, obtained by *Berthelot and Luca*[4] from glycerol and acetylchloride, boils under a pressure of 740 mm. at 202°-203° C.; $d^{11} = 1{\cdot}283$ (*Truchot*[5]).

β-Lauro-α-γ-dichlorohydrin, $CH_2.Cl.CH.(O.C_{12}H_{23}O).CH_2.Cl$ (*Grün*[6]), is a yellow mobile oil, soluble in the usual organic solvents.

β-Myristo-α-γ-dichlorohydrin, $CH_2Cl.CH.(O.C_{14}H_{27}O).CH_2Cl$ (*Grün and Schreyer*[7]), obtained from myristyl chloride and α-γ-dichlorohydrin, forms transparent crystals melting at 20° C.

α-β-Dichlorohydrin, $CH_2Cl.CHCl.CH_2OH$, obtained by passing chlorine gas into allyl alcohol (*Tollens*[8]), boils at 182° C.; $d^{11{\cdot}5} = 1{\cdot}3681$.

Ester of α-β-Dichlorohydrin

γ-Lauro-α-β-dichlorohydrin, $C_3H_5.Cl.Cl.(O.C_{12}H_{23}O)$, is prepared from α-lauro-γ-monochlorohydrin by digesting with thionylchloride (*Grün and Skopnik*[9]).

α-β-γ-Trichlorohydrin, $CH_2Cl.CHCl.CH_2Cl$, is obtained by saturating a mixture of 5 volumes of concentrated glycerin and 4 volumes of glacial acetic acid with hydrochloric acid gas, distilling to 130° C., washing the residue (crude dichlorohydrin) with water and soda, drying over calcium chloride, and digesting with phosphorus pentachloride (*Fittig and Pfeffer*[10]).

Bromohydrins

α-Monobromohydrin, $CH_2Br.CH(OH).CH_2OH$, is obtained from glycerol and phosphorus tribromide (*Berthelot and Luca*).

α-γ-Dibromohydrin, $CH_2Br.CH(OH).CH_2Br$, is obtained from glycerol and phosphorus tribromide (*Berthelot and Luca*), or from glycerin and bromine (*Barth*[11]).

α-β-Dibromohydrin, $CH_2Br.CHBr.CH_2OH$, is obtained from allyl alcohol and bromine by allowing 60 grams of bromine to drop within three to four hours into a cooled solution of 20 grams of allyl alcohol in 100 grams of ethyl alcohol and 100 grams of carbonbisulphide.

Tribromohydrin, $CH_2Br.CHBr.CH_2Br$, is obtained by digesting allyl alcohol with bromine (*Tollens*[12]).

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[1] *Liebig's Annal.* 122, 73.

[2] *Ibid.* 168, 43.

[3] English patent 25,246, 1911.

[4] *Ann. de Chim. et de Phys.* [3], 52, 459.

[5] *Liebig's Ann.* 138, 297.

[6] *Berichte*, 1910, 1289.

[7] *Berichte*, 1912, 3424.

[8] *Liebig's Annal.* 156, 164.

[9] *Berichte*, 1909, 3751.

[10] *Liebig's Annal.* 135, 359.

[11] *Ibid.* 124, 349.

[12] *Ibid.* 156, 168.

Other esters of glycerol which appear to be acquiring commercial importance, especially for pharmaceutical purposes, are: *Glyceromono-o-chlorophenylester*, $CH_2.(O.C_6H_4Cl)CH.(OH).CH_2(OH)$; *glyceromono-p-chlorophenylester*;[1] *glycerylchloroxy-isobutyrate*;[2] *glycerodimorphine ester*;[3] *glyceromonocinnamin*;[4] *glyceryllactate*;[5] *glycerylsalicylic ester*.[6]

For compounds formed from glycerol and amino acids, *E. Abderhalden and M. Gugenheim*.[7]

Polyglycerols

It has been stated above that on heating glycerol rapidly, polyglycerols are formed, no doubt, by the combination of several molecules of glycerol with loss of water. Polyglycerols are formed on a large scale on distilling glycerin, when the bulk of the polyglycerols remains in the still (see Vol. III. Chap. XV. "Glycerin Manufacture").

Lourenço[8] effected the condensation of glycerol to polyglycerols by heating glycerol with monochlorohydrin. By fractionating *in vacuo* the product of reaction, *diglycerol*, $C_6H_{14}O_5(=2C_3H_8O_3-H_2O)$, boiling at 220°-230° C. under a pressure of 10 mm., and *triglycerol*, $C_9H_{20}O_7$ $(=3C_3H_8O_3-2H_2O)$, boiling at 275°-285° C. under 10 mm. pressure, are obtained.

The amount of polyglycerols formed by heating glycerol to 290°-295° C. for seven to eight hours was usually stated to vary from 25-45 per cent of diglycerol and 4-6 per cent of triglycerol. Recently *Claessen*,[9] by heating commercial glycerin for five to six hours to 290°-295° C. (under a reflux condenser, the water vapours being allowed to pass away), obtained 55-65 per cent of diglycerol which could be distilled off at a pressure of 8-10 mm. between 245° and 250° C. On adding, however, 0·5 per cent of caustic alkali and heating to 275°-280° C., there were formed, within thirty minutes, 70 to 80 per cent of diglycerol and higher polyglycerols (*Claessen*[10]). (Cp. also Vol. III. "Glycerin Manufacture.")

Diglycerol, like glycerol itself, can be nitrated with a mixture of nitric and sulphuric acids, when tetranitrodiglycerol, $C_6H_{10}N_4O_{13}$, is formed. The tetranitroglycerol remains viscous at very low temperatures; it is claimed that by adding a small quantity to the ordinary nitroglycerin the freezing point of the latter is reduced considerably (cp. Vol. III. "Dynamite Glycerin").

Methods for the quantitative determination of glycerol will be described in Chapter VI. With a view to determining the glycerol in a direct manner by isolating a derivative of glycerol which would permit its quantitative determination, *Niemilowicz*[1] studied the action of hydrobromic acid on a solution of glycerol in concentrated sulphuric acid. There are, however, two products formed: tribromopropaldehyde and tribromopropionic acid. A direct method of determining glycerol in substance by extraction with acetone was worked out by *Shukoff and Schestakoff* (see Chap. VI.).

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[1] Poulenc Frères and E. Fourneau, German patent 219,325; cp. also F. Ehlotzky, *Monatsh. f. Chem.*, 1909 (30), 663.

[2] Poulenc Frères, French patent 430,820.

[3] Poulenc Frères, French patent 430,819.

[4] Callsen, U.S.A. patent 999,955.

[5] Kalle, German patent 216,917.

[6] C. Sorger, English patent 3367, 1907, French patent 373,854.

[7] *Zeits. f. physiol. Chem.*, 1910 (65), 53.

[8] *Ann. de Chim. et de Phys.* (3), 67, 299.

[9] German patent 181,754.

[10] German patent 198,768.

On heating glycerol with the theoretical amount of hydriodic acid allyliodide and propylene are formed. In the presence of an excess of hydriodic acid, isopropyliodide is obtained with smaller quantities of propylene, their quantities varying according to the conditions of the experiment. *Zeisel and Fanto*[2] published some experiments purporting to show that glycerol can be converted into isopropyliodide quantitatively, if an excess of strong hydriodic acid, specific gravity 1·7 (or even 1·9), be used. They endeavoured to base on this the quantitative determination of pure glycerol, by distilling the isopropyliodide formed into an alcoholic solution of silver nitrate. *Lewkowitsch*[3] has shown that when applied to concentrated glycerol solutions, the method yields results far below the true ones. Several observers who applied this method to very dilute solutions attach importance to the method. *Willstätter and Madinaveitia*[4] state that if hydriodic acid of 1·8 specific gravity be employed reliable results are obtained. How far the multiplication of unavoidable errors by the enormous factors of 300 to 600 help to lead to favourable results has not been yet investigated (cp. Chap. VI. " Glycerol ").

With regard to the manufacture and uses of glycerol see Vol. III. Chap. XV. " Glycerin Manufacture."

VI.—Alcohols of the Cyclic Series

Sterols[5]

The members of this group contain an alcoholic OH group, but differ chemically from the alcohols of the aliphatic series most essentially (for the purposes of fat analysis) in that they are not converted into fatty acids having the same number of carbon atoms by heating with potash-lime or soda-lime (*Lewkowitsch*; see Chap. VIII.).

The sterols seem to play an important, although not yet fully understood *rôle* in the internal economy of plants and animals. Cholesterol in especial seems to exert an antitoxic function towards the hæmolytic action of poisons, such as saponin.

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[1] *Journ. Chem. Soc.* Abstr., 1890, 861.

[2] *Zeit. f. d. landw. Versuchsw. in Oesterr.*, 1902, 1.

[3] *Analyst*, 1903, 108.

[4] *Berichte*, 1912, 2825.

[5] This name was proposed by Abderhalden, *Lehrbuch d. physiol. Chem.*, 1909, 154. It has been adopted here, as it appears to be a very suitable name.

General Reaction of the Sterols

The sterols:—cholesterol, phytosterol (sitosterol), stigmasterol, brassicasterol, and coprosterol can be detected qualitatively by means of an alcoholic digitonin solution. Thus on adding a few drops of a 1 per cent alcoholic solution of digitonin,[1] $C_{55}H_{94}O_{28}$, to a solution of 0·001 grm. of cholesterol in 1 c.c. of 95 per cent alcohol, almost immediately a precipitate is obtained, which consists of a chemical individual formed by the combination of one molecule of digitonin and one molecule of cholesterol—no separation of water taking place—thus: $C_{27}H_{46}O + C_{55}H_{94}O_{28}$ (digitonin) $= C_{82}H_{140}O_{29}$. The addition product is insoluble in water, acetone, and ether, slightly soluble in cold 95 per cent, more readily soluble in boiling absolute alcohol, in methyl alcohol, glacial acetic acid, and especially pyridine. On boiling the compound with xylene, it is split into its components; the sterol passes into the xylene, the digitonin remaining undissolved. This property of the sterols permits their ready separation from hydrocarbons and aliphatic alcohols.

The esters of the sterols do not form compounds with digitonin; it is therefore possible to differentiate qualitatively cholesteryl, etc. esters from cholesterol, etc., and to separate quantitatively the free alcohols from their esters.[2]

In the case of physiological preparations the digitonin method is stated to yield good results.[3] In the case of oils and fats, however, the complete separation of the sterols appears to depend on the nature of the uncrystallisable substances accompanying the sterols; if those substances are of resinous nature, the separation becomes difficult and requires repeated treatment, which can only lead to trustworthy results if sufficiently large amounts of "unsaponifiable matter" is available (*Lewkowitsch*).

The subdivision of the Sterols into Zoosterols and Phytosterols has been referred to above (p. 4).

(*a*) *Zoosterols*

(1) CHOLESTEROL, $C_{27}H_{46}O$

Cholesterol, discovered by *Conradi* (1775) and by *Gren* (1788) in biliary calculi, occurs in considerable quantities in wool fat. It is frequently met with in the animal organism; the biliary calculi are almost wholly composed of cholesterol. Its presence has been further proved in human bile,[4] in blood, in the brain, in hair, in the epidermis, in milk, in various morbid products of the animal body, and in the yolk of eggs.[1]

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[1] For the preparation of digitonin see Th. Panzer, *Chem. Zentralbl.*, 1912 (ii.), 540.

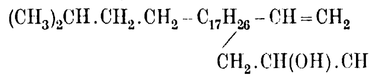
[2] Windaus, *Berichte*, 1909, 238; *Zeits. f. physiol. Chem.*, 1910 (65), 110.

[3] Cp. A. Lapworth, *Journ. Path. Bact.*, 1911 (15), 254.

[4] A certain amount of cholesterol is discharged together with the bile into the intestines, and is there attacked by the bacteria occurring in the intestines, whereby amongst other products coprosterol (p. 279) is formed.

All animal oils and fats contain small quantities of cholesterol, *hence the presence of cholesterol in an oil or fat points to its animal origin.* Its presence has been proved not only in the mammiferæ and birds, but also in reptiles, fishes (see "Fish, Liver, and Blubber Oils," Vol. II. Chap. XIV.), molluscs, crustaceæ, insects (see "Chrysalis Oil," Vol. II. Chap. XV.), worms, and cœlenterata. The echinodermata[2] and sponges contain a body similar in type to cholesterol. The quantity of cholesterol in animal oils and fats varies from 0·2 to about 1·0 per cent.

The chemical formula of cholesterol was for a considerable time in dispute. *Reinitzer*[3] considered that three homologous cholesterols, $C_{25}H_{42}O$, $C_{26}H_{44}O$, and $C_{27}H_{46}O$, exist. Cholesterol prepared from biliary calculi has the composition $C_{27}H_{46}O$. *Mauthner and Suida* favoured the formula $C_{27}H_{44}O$, but *Windaus*, as also *Diels and Abderhalden*, demonstrated that the formula $C_{27}H_{46}O$ is the correct one for cholesterol.[4] According to the latest researches of *Windaus*,[5] the following extended formula would so far explain best the constitution of cholesterol :—



$$\begin{array}{l}(CH_3)_2CH.CH_2.CH_2-C_{17}H_{26}-CH=CH_2\\ \qquad\qquad\qquad\qquad\quad / \\ \qquad\qquad\qquad\quad CH_2.CH(OH).CH_2\end{array}$$

C. Dorée and J. A. Gardner[6] confirm *Windaus*' conclusion, that one double bond in cholesterol is contained in a terminal vinyl group. From the fact that cholesterol absorbs two molecules of ozone it would follow that cholesterol contains two double bonds (see p. 145).

Windaus and Stein,[7] as also *Mauthner*,[8] arrive at the conclusion that cholesterol is a complicated terpene compound. This has been confirmed by *Schrötter and Weitzenböck*,[9] who obtained from cholesterol *rhizocholic acid*,[10] $C_8H_6O_7$, the same acid which is furnished (although in very small quantities only) by camphor and by oil of turpentine.

Cholesterol crystallises from chloroform in anhydrous needles (cp. Chap. IX.), melting at 148·4°-150·8° C. corr. (*Böner*). *Polenske* found for 284 cholesterols, isolated from 254 different specimens of lards, the following (corrected) melting points :—

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[1] Cp. A. Windaus, *Arch. d. Pharm.*, 1908, 117. C. Dorée and J. A. Gardner, *Journ. Chem. Soc.*, 1908, 625 ; L. Wacker, *Zeits. f. physiol. Chem.*, 1912 (80), 383.

[2] Cp. A. Welsch, *Inaug. Dissert.*, Offenbach a/M., 1909 ; Dorée, *Biochem. Journ.*, 1909 (4), 72.

[3] *Journ. Soc. Chem. Ind.*, 1888, 585. Cp. *Jahrbuch d. Chem.*, 1896, vi. 360.

[4] Menozzi, who showed that milk- and egg-yolk cholesterol is identical with bile cholesterol, still retains the formula $C_{26}H_{43}OH . H_2O$ (cp. Bombicesterol). L. Tschugajeff and A. Gasteff furnished some further proof (*Berichte*, 1909, 4634) for the composition $C_{27}H_{46}O$.

[5] *Berichte*, 1908, 2568 ; 1909, 3770.

[6] *Proc. Chem. Soc.*, 1908, 173 ; *Trans. Chem. Soc.*, 1908, 1328.

[7] *Inaug. Dissert.*, 1905, Freiburg i/B.

[8] *Monatsh. f. Chem.*, 1907, 1113.

[9] *Ibid.*, 1908, 395.

[10] This is the second instance of the occurrence of a derivative of terpenes from products formed in the animal organism, the first being the occurrence of muscone in musk (Walbaum, *Journ. f. prakt. Chem.* 73, 488).

No. of Samples.	Melting Point. °C.
2	145
15	146-146·5
36	146·5-147
185	147-148
15	148
1	148·5

From its hot alcoholic[1] solution cholesterol crystallises in laminæ, which are discerned under the microscope as very thin plates, frequently showing re-entering angles. These plates appear to be rhombic, but are most likely triclinic (*Bömer*). Illustrations of these crystals will be found in Chap. IX. The crystals contain one molecule of water, which evaporates on prolonged standing over sulphuric acid, and more quickly, at a temperature of 100° C.

Cholesterol is insoluble in water,[2] and very sparingly soluble in cold dilute alcohol. It dissolves in 9 parts of boiling alcohol of specific gravity 0·87, and in 5·55 parts of boiling alcohol of specific gravity 0·83. 10 c.c. of absolute alcohol dissolve 0·1916 gr. (*Polenske*). Ether, carbon bisulphide, and chloroform dissolve it easily, acetone and petroleum ether less readily. According to *Bömer*,[3] 100 c.c. of petroleum ether, of specific gravity 0·7522, boiling from 35° to 85° C., dissolve at 19° C. 0·8320 grm., and at 23° C. 1·0380 grms. According to *Polenske*, 10 c.c. of petroleum ether boiling below 50° C. dissolve 0·086 to 0·095 grm. Cholesterol dissolves sparingly in cold glacial acetic acid, more easily in the hot, whilst it is slowly converted into cholesteryl acetate.

Cholesterol is lævo-rotatory. *Hesse* gives $[\alpha]_D^{15} = -31{\cdot}12^\circ$ $[c=2$ for ether$]$ $[\alpha]_D = -(36{\cdot}61^\circ + 0{\cdot}249c)$ $[c=8$ for chloroform$]$. *Menozzi* found $[\alpha]_D^{15} = -34{\cdot}3^\circ$ (and $-35{\cdot}8^\circ$) in chloroform solution. For acetic ester solution *Diels and Linn* found $[\alpha]_D^{20} = -25{\cdot}6^\circ$.

On heating cholesterol for one hour at 350° C., a product exhibiting strong dextro-rotation is obtained; if the cholesterol be heated to 300° C. only, no sensible decrease of the original lævo-rotation is observed (*Engler*[4]).

If cholesterol be heated carefully under ordinary pressure, it volatilises without undergoing decomposition; *in vacuo* it can be readily distilled unchanged. *Diels and Linn*[5] observed that on heating cholesterol to 300°-320° C. strong evolution of hydrogen occurs. This reaction only takes place in the presence of a catalyst, such as a small quantity of iron (or zinc) which clings tenaciously to cholesterol prepared from the yolk of eggs. Perfectly pure cholesterol does not show this behaviour. On subjecting cholesterol to destructive distillation[6] optically active substances (hydrocarbons ?) are formed (cp. Vol. III. Chap. XV.).

Engler[4] observed that on repeatedly distilling cholesterol under pressure the dextro-rotation decreases, finally to disappear entirely. The same change takes place on heating cholesterol without subjecting it to distillation. A product obtained by distilling, three times successively, 20 grams of cholesterol, and having a dextro-rotation of 112° in a 200 mm. tube of a saccharimeter, yielded on fractional distillation *in vacuo* 9 distillates having the following properties :—

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[1] For colloidal solutions of cholesterol see J. R. Partington, *Journ. Chem. Soc.*, 1911, 316; O. Porges and Neubauer, *Biochem. Zeits.*, 1908 (7), 152.

[2] Porges and Neubauer (*Biochem. Zeits.* 7, 152) were able to prepare a colloidal solution of cholesterol.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898, 37.

[4] *Zeits. f. angew. Chem.*, 1908, 1594.

[5] *Berichte*, 1908, 260.

[6] Heintz, *Liebig's Annal.* 76, 366.

Fraction.	Boiling Point under 15 mm. pressure.	Saccharimeter "degrees" in a 200-mm. tube.	Appearance.
	° C.		
1	100-193	−1·2	Thin liquid ; pale yellow
2	193-230	+57·6	Thin liquid ; pale yellow
3	230-245	+88·0	Thicker ; yellow
4	245-250	+104·0	Thicker ; dark yellow
5	250-258	+108·0	Viscous ; pale brown
6	258-270	+118·0	Viscous ; pale brown
7	270-275	+128·0	Viscous ; brown
8	275-280	+144·0	Viscous ; brown
9	280-288	+164·0	Viscous ; dark brown

It should be pointed out that the distillate exhibiting the highest dextro-rotation still contained about 2 per cent of oxygen, whereas pure cholesterol contains 4·2 per cent of oxygen. The chemical composition of the distillates is unknown ; they certainly do not consist exclusively of hydrocarbons. According to *Steinkopf*,[1] even those fractions which are obtained by fractional distillation of cholesterol under ordinary pressure and exhibit the strongest dextro-rotation, still contain undecomposed cholesterol, as ascertained by the digitonin reaction.

On adding bromine to a solution of cholesterol in carbon bisulphide, cholesteryl dibromide, $C_{27}H_{46}O.Br_2$, is formed (*Wislicenus and Moldenhauer*[2]). With *Hübl's* iodine solution an iodochloro-addition product is obtained (*Lewkowitsch*[3]). Theory requires the iodine value 65·8. *Lewkowitsch* found for a specimen of gall cholesterol 67·3-68·09 ; cholesterol may thus be estimated quantitatively ; *Wijs'* iodine solution, on the contrary, yields erratic results (see Chap. IX.). If only half the theoretical quantity of bromine be added, crystals having the composition $C_{27}H_{46}OBr_2 + C_{27}H_{46}O$ and melting at 112° C. separate.[4] The two atoms of bromine can be eliminated from the dibromide $C_{27}H_{46}OBr_2$ with regeneration of cholesterol by careful treatment with zinc dust or sodium amalgam.

Cholesteryl dibromide is sparingly soluble in a mixture of ether and glacial acetic acid. A mixture of 50 c.c. of ether and 50 c.c. of glacial acetic acid at 20° C. dissolves 0·6 grm., and a mixture of 40 : 60 only 0·25 grm. In the presence of a small amount of water the solubility is still further reduced. (Difference from sitosteryl dibromide.[5]) *Menozzi* gives the melting point of cholesterol dibromide as 111° C., and *Windaus*,[1] 124°-125° C. The author is unable to confirm these statements, as a specimen of pure dibromide examined in a capillary tube blackened at 108°-109° C. *Dorée*,[2] on the other hand, gives as the melting point of the dibromide 123° C. $[\alpha]_D = -42{\cdot}85°$ (*Menozzi*). The above-given data may perhaps be explained by assuming the existence of several isomeric dibromides.

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[1] *Chem. Zeit.*, 1912, 653 ; cp. also W. Steinkopf and E. Blümner, *Journ. f. prakt. Chem.*, 1911 (84), 460.

[2] *Liebig's Annal.* 146, 175.

[3] *Journ. Soc. Chem. Ind.*, 1892, 43.

[4] Cloëz, *Compt. rend.*, 1897 (124), 864.

[5] Windaus, *Berichte*, 1906, 518 ; *Chem. Zeit.*, 1906, 1011.

Cholesteryl bromide, prepared by the action of phosphorus tribromide on cholesterol in benzene solution crystallises in nacreous platelets, m.p. 98° C. On melting this dibromide and allowing it to cool again, a particularly fine play of colour is obtained. $[\alpha]^{19{\cdot}5}_D = -19{\cdot}14°$.

It reacts with bromine in acetic acid to form tribromocholestan, $C_{27}H_{43}Br_3$, which crystallises in well-formed, short prisms, melting at 111°-112° C. $[\alpha]^{19}_D = -49{\cdot}82°$ (without mutarotation) (*R. Kolm*[3]).

With phosphorous tri-iodide, cholesteryl iodide was obtained (*R. Kolm*[3]).

According to *Dorée and Gardner*,[4] cholesterol absorbs, on treatment with ozone in chloroform solution, 1 molecule of ozone, yielding the ozonide $C_{27}H_{46}O.O_3$, having $[\alpha]^{20}_D = +14{\cdot}51°$. According to *Molinari and Fenaroli*, however, cholesterol assimilates two molecules of ozone (theory 24·85 per cent; found 25·00 and 24·70 per cent). It would thus seem to follow that cholesterol contains two pairs of doubly-linked carbon atoms. Hence the statement by *Windaus and Hauth*, that the α-cholestanol (cyclocholesterol), obtained on treating cholesterol with metallic sodium (see below), is a saturated substance, may require qualification.[5]

Cholesterol dissolves in concentrated sulphuric acid;[6] on warming the mixture, it is converted into a hydrocarbon $C_{26}H_{42}$ (?)—cholesterilene.[7] (Difference from aliphatic alcohols.) As a further important difference from aliphatic alcohols, it should be noted that on heating cholesterol with soda-lime (*Lewkowitsch*[8]) no fatty acids are formed. On heating cholesterol with normal alcoholic potash on the water-bath under a reflux condenser for three to four hours, 20-25 per cent of a hydrated cholesterol is said to be formed. This product is, however, not obtained if cholesterol be heated with normal or 1½ normal potash in a sealed tube at 112°-115° C.[9]

By exposure to light and air cholesterol appears to undergo some change, the melting point becomes lower, the solubility is changed considerably, and the colour reactions (see below) are very indefinite

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[1] *Arch. d. Pharm.*, 1908, 122.

[2] *Biochem. Journ.*, 1909 (4), 77.

[3] *Monatsh. f. Chem.*, 1912 (33), 447.

[4] *Journ. Chem. Soc.*, 1908, 1332; cp. Diels, *Berichte*, 1908, 2596.

[5] Cp. *Berichte*, 1908, 2785; cp. also Dorée.

[6] With regard to the behaviour of cholesterol to concentrated sulphuric acid in the presence of metallic mercury, whereby rhizocholic acid is formed, see Schrötter, Weitzenböck, and Witt (*Monatsh. f. Chem.*, 1908, 245); cp. also *Berichte*, 1908, 1561, and *Zeits. f. angew. Chem.*, 1908, 2146.

[7] Zwenger, *Annalen*, 66, 5; 69, 347; Mauthner and Suida, *Monatsh. f. Chem.* 17, 33; cp. also Cochenhausen, *Dingl. Polyt. Journ.*, 1897 (303), 284.

[8] *Berichte*, 1892, 66; *Journ. Soc. Chem. Ind.*, 1896, 84.

[9] Darmstaedter and Lifschütz, *Berichte*, 1898, 1126.

(*Schulze and Winterstein*[1]). This is confirmed by the author's experience. Thus a sample of cholesterol from gallstones had lost its ready solubility in the course of twelve years, one part of cholesterol requiring for complete solution more than 100 parts of anhydrous ether; furthermore, an old specimen[2] of well-crystallised cholesterol had the melting point of 119° C. only. It is not certain whether cholesterol undergoes these changes owing to oxidation. For the oxidation products of cholesterol compare Windaus, *Archiv der Pharm.*, 1908, 117. *Lifschütz's* statements with regard to the oxidation of cholesterol and its oxidation products[3] have been severely criticised by *Windaus.*[4]

On heating cholesterol with anhydrous copper sulphate to 200° C., cholesterylether, $(C_{27}H_{43})_2O$ [more correctly $(C_{27}H_{45})_2O$], is obtained, cholesterilene being formed as a by-product (*Mauthner and Suida*[5]). This ether melts at about 195° C. and crystallises from a mixture of benzene and absolute alcohol in the form of needles. (Difference from phytosterylether, *Holde.*[6])

Cholesterol does not readily assimilate two atoms of hydrogen on treatment with zinc dust and acetic acid or sodium amalgam. On boiling it in amylalcoholic solution with sodium amalgam, a saturated alcohol, $C_{27}H_{48}O$, α-cholestanol (cyclocholesterol, *Diels and Abderhalden*; *Neuberg*[7]), differing from coprosterol (see below), is obtained. In *Windaus'* opinion, α-cholestanol is not a reduction product but a compound having the same composition as cholesterol itself, viz. $C_{27}H_{46}O$; the formation of cholestanol must be ascribed to a molecular rearrangement, due to the conversion of the olefinic linkage into a cyclic one (cp., however, the ozone compound, above). The catalytic reduction of cholesterol by means of hydrogen in presence of platinum black (*R. Willstätter and E. W. Mayer*[8]) yielded a dihydro-cholesterol (β-cholestanol). *Wilenko and Motylewski*[9] obtained by treating cholesterol with sodium in amylalcohol solution dihydrocholesterol, an alcohol resembling coprosterol (described as *l* coprosterol; crystallising in long needles, melting at 86°-87° C., $[\alpha]_D = -14{\cdot}3°$) and an alcohol, termed γ-cholesterol ($C_{27}H_{46}O$, melting at 135°-137° C.; some specimens were dextro-rotatory, others inactive. The acetate melts at 100°-102° C.).

On treating cholesterol with phosphorus pentachloride it is converted into cholesterylchloride; this is reduced by boiling with sodium (in amyl alcohol solution) to cholestene, $C_{27}H_{46}$, which is still optically active.

Colour Reactions of Cholesterol (cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 144, and Windaus, *Arch. der Pharm.*, 1908, 123).

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[1] *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1904 (53), 631; 1906 (48), 546.

[2] The author obtained this specimen from B. E. R. Newlands, who had prepared it from gallstones in 1859.

[3] *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1907 (50), 436; (53) 141; 1908 (58), 175.

[4] *Arch. d. Pharm.*, 1908, 149.

[5] *Monatsh. f. Chem.* 17, 38; Holde, *Zeits. f. angew. Chem.*, 1906, 1608.

[6] *Zeits. f. angew. Chem.*, 1906, 1609.

[7] *Berichte*, 39, 1155; cp. also Pickard and Yates, *Journ. Chem. Soc.*, 1908, 1678.

[8] *Bull. Acad. Science*, Krakow, 1908, 837.

[9] *Berichte*, 1908, 2199.

The following two colour reactions were recommended by *Schulze* :—

1. If a minute quantity of cholesterol be carefully heated to dryness with a drop of concentrated nitric acid on a crucible cover, a yellow stain is obtained ; on pouring a little ammonia on to it, a yellowish-red tint is produced.

2. If a small amount of cholesterol be triturated on a crucible cover with one drop of a mixture, consisting of three measures of concentrated hydrochloric acid and one measure of a 10 per cent solution of ferric chloride, a violet-red colouration is produced, changing to blue on evaporation to dryness. It must, however, be remembered that oil of turpentine, camphor, and other substances behave in a similar manner.

A very delicate and characteristic reaction, described by *Hager*, was modified by *Salkowski*, as follows :—A few centigrams of cholesterol are dissolved in 2 c.c. of chloroform, an equal volume of concentrated sulphuric acid is added, and the mixture shaken. The chloroform solution immediately becomes coloured blood-red, afterwards cherry-red and purple ; the last tint remains for several days. (The sulphuric acid layer under the chloroform shows sometimes a strong green fluorescence.[1]) On pouring a few drops of the purple chloroform layer into a porcelain basin, the red colour changes rapidly to blue, green, and finally to yellow. On diluting the purple solution with more chloroform, it becomes nearly colourless or acquires an intense blue colour ; if it now be shaken again with the sulphuric acid, the former colouration reappears. These changes of colour are said to be due to traces of water in the chloroform.[2]

If a chloroform solution of cholesterol prepared from fats be shaken with concentrated sulphuric acid, the blue colouration is noticed at once ; this indicates the presence of so-called " lipochromes," which have been shown to occur in cod-liver oil, the fat of the yolk of eggs, palm oil, and in small quantities in cow butter. But even in these cases the red colouration soon appears.

Salkowski later recommended the following *modus operandi* :—Dissolve a small quantity of cholesterol in chloroform, drop the solution on filter paper, dry the latter and pour some concentrated sulphuric acid on it. The cholesterol drops become lemon-yellow ; on pouring off the sulphuric acid, the yellow colour changes to reddish or rose-red and disappears immediately on adding water.[3]

Liebermann's " cholestol " reaction is very characteristic, and is shown by the minutest quantities of cholesterol. A solution of cholesterol in acetic anhydride gives a violet-pink colouration[4] on adding drop by drop concentrated sulphuric acid. Sharper still is the modified form of this test as proposed by *Burchard* : Dissolve a little cholesterol in 2 c.c. of chloroform, add 20 drops of acetic anhydride and 1 drop of concentrated sulphuric acid.

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[1] In the case of wool fat cholesterol this green fluorescence is, in the author's opinion, due to the presence of isocholesterol.

[2] According to Herbig (*Dingl. Polyt. Journ.*, 1897 (303), 191), cholesteryl palmitate and cholesteryl cerotate give the same colour reaction.

[3] *Zeits. f. physiol. Chem.*, 1908 (57), 515.

[4] Wool fat cholesterol does not show the violet-pink colouration given by gallstone cholesterol, but becomes red at once.

It should be noted that rosin acids (colophony), terpenes, and other substances give the same or very similar reactions.[1] It is therefore not advisable to rely exclusively on colour reactions [2] for the purposes of identifying cholesterol.

With regard to the detection and isolation of cholesterol from animal oils and fats, its quantitative determination, and separation from phytosterol, cp. Chap. VI., Chap. IX., and Chap. XI.

Esters of Cholesterol

Cholesteryl formate, $C_{27}H_{45}O.CHO$, crystallises in long, fine needles melting at 96·8° C. (corr.) (*Bömer*). $[\alpha]_D^{15} = -52·5°$ (cholesterol from egg yolk); $[\alpha]_D^{14} = -51·83°$ (from milk); $[\alpha]_D^{13} = -51·48°$ (from bile) (*Menozzi* [3]).

Cholesteryl acetate, $C_{27}H_{45}O.C_2H_3O$, is prepared by boiling cholesterol with one and a half times its quantity of acetic anhydride in a flask connected with an inverted condenser. This reaction may also be used for the quantitative determination of cholesterol (*Lewkowitsch* [4]). Cholesteryl acetate crystallises in small needles, nearly insoluble in cold, and sparingly soluble in boiling alcohol; they dissolve very readily in petroleum ether boiling below 50° C. The crystals melt at 114° C.; 114·3°-114·8° C. (corr.) (*Bömer*). On solidifying, the crystals display colours (see *Jäger* below). $[\alpha]_D^{14} = -42·7°$ (from milk); $-42·5°$ (from bile) (*Menozzi* [3]).

Cholesteryl propionate, $C_{27}H_{45}O.C_3H_5O$, crystallises in the form of very fine needles; it melts at 98° C. (*Obermüller*), 96·8° C. (corr.) (*Bömer*).

Cholesteryl (normal) *butyrate*, $C_{27}H_{45}O.C_4H_7O$, crystallises in the form of short, fine needles melting at 95°-96·8° C. (corr.) (*Bömer*).

Cholesteryl isobutyrate, $C_{27}H_{45}O.C_4H_7O$, melts at 127° C. This ester furnishes the best-defined crystals amongst all cholesteryl esters, and does not form "liquid crystals." Hence it melts sharply; m.p. 127° C. (*Jäger*).

Cholesteryl isovalerate, $C_{27}H_{45}O.C_5H_9O$, melts at 114° C. $[\alpha]_D^{20} = -32·7°$ (*E. Abderhalden and K. Kautzsch* [5]).

Cholesteryl laurate, $C_{27}H_{45}O.C_{12}H_{23}O$, crystallises in slender needles, melting at 110° C., and after sintering at 78·5-79·5. $[\alpha]_D^{20} = -24·2°$.

For *cholesteryl palmitate, stearate, oleate,* and *cerotate* see p. 66.

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[1] Cp. Lewkowitsch, *Berichte*, 1892, 66.

[2] For Tschugajeff's colour reactions with trichloro-acetic acid, described by Lifschütz (*Berichte*, 1908, 253), and Denigès (*Chem. Revue*, 1904, 231), the reader must be referred to the original papers, as these reactions are given by other substances as well as by cholesterol. The same strictures apply to the test proposed by Neuberg and Rauchwerger (*Festschrift f. E. Salkowski*, p. 281); *Zeits. f. physiol. Chem.* (12), 355, and later on again by Udransky; cp. also Ottolenghi (*Atti R. Accad. dei Lincei*, 1906, 15, i. 44, and *Biochem. Zeits.*, 1908 (xiv.), 351.

[3] *Atti R. Accad. dei Lincei*, 1903 (12), i. 126; *ibid.*, 1908 (17), i. 91.

[4] *Berichte*, 1892, 66; *Journ. Soc. Chem. Ind.*, 1896, 14.

[5] *Zeits. f. physiol. Chem.*, 1910 (65), 69.

Cholesteryl benzoate, $C_{27}H_{45}O.C_7H_5O$, is formed by heating cholesterol with benzoic anhydride in a sealed tube to a temperature of 200° C. or by dissolving cholesterol in pyridine and adding a solution of benzoyl chloride in pyridine (*Dorée*[1]). It is nearly insoluble in boiling alcohol, 100 c.c. of absolute alcohol hold at 20° C. 0·12 grm. in solution (*Dorée*[1]), and crystallises from ether in rectangular plates melting at 150°-151° C. (*Schulze*), 145·5° C. (*Obermüller*), 148·4° C. (corr.) (*Bömer*), 146° C. (*Menozzi*). $[\alpha]_D^{13} = -15·1°$ (from milk), $-15·4°$ (from bile). *Monobromo-cholesterylbenzoate*, $C_{27}H_{44}O.Br.C_7H_5O$, melts at 136° C.[2] $[\alpha]_D^{15} = -15·1°$ (in chloroform; *Menozzi*, cp. *Moreschi*[3]). *C. Dorée and C. Stotesbury*[4] showed that on brominating the benzoate two substances are formed, viz. the monobromide (melting at 139° C.) and the dibromide (melting at 168° C.).

Cholesteryl salicylate,[5] $C_{27}H_{45}O.(C_6H_4COO)OH$, melts at 173° C.

For other esters and the several liquid phases and the colour changes which all the cholesteryl esters exhibit, see *Jäger*,[6] *Wallerant*,[7] *Lehmann*,[8] *Ada Prins*,[9] *P. Gaubert*,[10] *C. P. White*.[11]

The separation of cholesterol from cholesterylesters is of importance to the physiological chemist.[12] This can be effected to some extent by means of aceto-ethylacetate, in which cholesterol is much less soluble than the cholesterylesters (*Liebreich*[13]). The separation is, however, best effected by means of the digitonin reaction (see above). For the separation from natural oils and fats *Windaus*[14] also suggested the employment of such ferments as would hydrolyse the glycerides, but leave the cholesterylesters unattacked. This method may be considered as superseded by the digitonin method.

(2) Isocholesterol, $C_{27}H_{46}O$[15]

This alcohol is isomeric with cholesterol, and resembles it in many respects. It occurs together with it in wool fat (*Hartmann*, *Schulze*; cp. also Vol. II. Chap. XIV.). Isocholesterol, isolated from its benzoate (*Schulze*[16]), crystallises from ether in fine needles melting at 137°-138° C. (140°-141° C. *Moreschi*[17]). It dissolves sparingly in cold, rapidly in boiling alcohol, from which it separates, on cooling, in a jelly-like mass. It is readily soluble in ether and in petroleum ether.

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[1] *Biochem. Zeits.*, 1909 (4), 75.

[2] Obermüller, *Zeits. f. physiol. Chem.*, 1891 (15), 37.

[3] *Atti R. Accad. dei Lincei*, 1910 (19), ii. 53.

[4] *Proc. Chem. Soc.*, 1912, 196.

[5] Golodetz, *Chem. Zeit.*, 1907, 1215. E. Artini, *Atti R. Accad. dei Lincei*, 1910 (v.), 19, i. 782.

[6] *Recueil des trav. chim. des Pays-Bas*, 1906, 334; *Chem. Weekblad*, 1907, i.; *Koningl. Akad. van Wetensch.*, Amsterdam, 1907, 359, 472.

[7] *Compt. rend.*, 1906 (143), 605.

[8] *Zeits. f. angew. Chem.*, 1906, 1641.

[9] *Zeits. f. phys. Chem.*, 1909 (67), 639.

[10] *Compt. rend.*, 1909 (149), 608.

[11] *Proc. Phys. Soc.*, 1908 (vi.), 38.

[12] Cp. Unna and Golodetz, *Biochem. Zeits.* 1909 (24), 484; 1910 (25), 425, and E. Salkowski, *ibid.*, 1910 (25), 427.

[13] Cp. also E. Salkowski, *Arbeiten a. d. phys. Institut. zu Berlin.*

[14] *Arch. d. Pharm.*, 1908, 125.

[15] The author adopts the same formula which has been established for cholesterol (*Berichte*, 1898, 1200).

[16] *Journ. f. prakt. Chem.* [2], 7, 163.

[17] *Atti R. Accad. dei Lincei*, 1910 (19), ii. 53.

A phytosterol isolated by *H. N. Cohen*[1] from African rubber (obtained from a *Euphorbia*) and melting at 141° C. is in *Cohen's*[2] opinion identical with isocholesterol, for on mixing a preparation of *Schulze's* original isocholesteryl benzoate with the benzoate of the rubber-phytosterol, as also by mixing isocholesterol obtained from isocholesteryl benzoate with the phytosterol from the rubber, no lowering of the melting points was observed. *Cohen* draws from these observations the important conclusion that no fundamental difference exists between " cholesterols " of animal and vegetable origins. In the author's opinion this conclusion does not appear to be sufficiently substantiated.

On treatment with hydrogen it does not form, like cholesterol and bombiscesterol, a dihydro-derivative (*Moreschi*[3]). According to *Darmstädter and Lifschütz*[4] it absorbs bromine readily ; the compound so obtained melts readily and forms with alcoholic potash a yellow solution turning green on boiling, and becoming yellow again on cooling (*Moreschi*).

Isocholesterol is optically active ; in contradistinction to cholesterol it is dextro-rotatory. $[\alpha]_D = +60°$ in ethereal solution (*Schulze*). $[\alpha]_D^{17} = +59{\cdot}1°$ in chloroform (*Moreschi*[3]).

On exposure to light isocholesterol, like cholesterol, undergoes a change. Thus a sample exposed for twenty years to the light melted at 112° C., after it had commenced to conglutinate at 95° C. A sample melting originally at 136°-137° C. had, after exposure to the light for a few months, the melting point of 119° C.

Colour Reactions of Isocholesterol.—Isocholesterol gives the same colour reaction with nitric acid and ammonia as does cholesterol. On adding one drop of concentrated sulphuric acid to a solution of isocholesterol in acetic anhydride, a yellow, and afterwards a reddish-yellow colouration is observed ; at the same time a strongly marked green fluorescence makes its appearance. The green colour becomes more distinct in the *Liebermann-Burchard* " cholestol " test (see above).

In a mixture of cholesterol and isocholesterol the colour reaction of the latter seems to prevail and to mask the violet-pink colouration due to cholesterol.

Isocholesteryl formate, $[\alpha]_D^{17} = +46\text{-}47°$ (*Moreschi*).

Isocholesteryl acetate, $C_{27}H_{45}O.C_2H_3O$, has been obtained as an uncrystallisable mass.

Isocholesteryl stearate, see p. 66.

Isocholesteryl benzoate, $C_{27}H_{45}O.C_7H_5O$, is a crystalline powder, consisting of very fine needles melting at 194°-195° C. (*Schulze*) ; 199° C. (*Moreschi*[3]). It dissolves sparingly in alcohol, more easily in hot acetone and in ether. $[\alpha]_D^{16}$ (in chloroform) $= +73{\cdot}33°$ (*Moreschi*[3]).

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[1] *Arch. d. Pharm.*, 1908 (246), 522.

[2] *Ibid.*, 1908 (246), 592.

[3] *Atti R. Accad. dei Lincei*, 1910 (19), ii. 53.

[4] *Berichte*, 1898, 97 ; 1122.

(3) BOMBICESTEROL ($C_{26}H_{44}O.H_2O$ [1]) $C_{27}H_{46}O$

This alcohol is stated to occur in the unsaponifiable matter of chrysalis oil, together with ordinary cholesterol (*Menozzi and Moreschi*[2]). After repeated crystallisation from alcohol it melted at 148° C. and had the specific rotation, in chloroform, $[\alpha]_D = -34{\cdot}91°$. Although the melting point, as also the optical rotation, is identical with that of cholesterol, and the composition is stated to be identical with that of bile cholesterol,[1] *Menozzi and Moreschi* maintain, on the strength of the crystalline form and the melting point of its acetate, viz. 129° C., that this alcohol differs from cholesterol. By treating the ethereal solution of the alcohol with one molecule of bromine (in glacial acid solution) a dibromo-derivative, melting at 111° C., is obtained (cp., however, p. 267).

According to *Molinari and Fenaroli*, bombicesterol absorbs 24·73 per cent of ozone, theory requiring for two pairs of doubly-linked carbon atoms 24·84 per cent. On reducing bombicesterol with hydrogen, dihydrobombicesterol is obtained. This alcohol is in chloroformic solution dextrorotatory, $[\alpha]_D^{19} = +19{\cdot}11°$; melting point 134° C. Bombicesterol can be separated from the concomitant cholesterol by means of the acetate, as also of the dibromide.

Formate, melts at 101° C. $[\alpha]_D^{17\cdot5°} = -47°$.

Acetate, melted in the impure state at 112°-114° C. After one crystallisation the melting point rose to above 120° C., and after repeated crystallisations to 129° C. (cp. Vol. II. Chap. XIV. "Chrysalis Oil"). $[\alpha]_D^{17\cdot5°} = -42{\cdot}7°$.

Benzoate, crystallises in laminæ, melting at 146° C. $[\alpha]_D^{20} = -14{\cdot}63°$.

(4) CLIONASTEROL

Clionasterol is an alcohol isolated from the tissue of sponges. It resembles both cholesterol and bombicesterol.

(*b*) *Phytosterols*

(1) SITOSTEROL, $C_{27}H_{46}O$ ($C_{27}H_{44}O$?)

Sitosterol, the "cholesterol of plants," is widely disseminated in the vegetable kingdom and occurs in all seeds and fruits, and is therefore also found in soil[3] (as an ester).

Until recently the chemistry of the several "phytosterols" isolated from different plants was only very incompletely known. At first the phytosterols were identified with cholesterol (*Beneke*,[4] *Lindenmayer*,[5] *Ritthausen*[6]) until *Hesse*[7] showed that the alcohol isolated from Calabar beans differs from cholesterol. A number of alcohols having the same composition were described under various names, such as caulosterol,[1] ergosterol,[2] hydrocarotol,[3] amycol,[4] agrosterol,[5] etc. *Bömer* obtained, from different oils, " phytosterols " differing in their melting points; since small quantities, such as he obtained, are very difficult to purify, and hence necessarily differ in their melting points, it is very probable that some of these alcohols described by him as separate individuals (such as peas-alcohol, beans-alcohol, etc.) are identical with sitosterol. Indeed *Windaus and Hauth* [5] are of the opinion that most of the " phytosterols " of the melting point 135° C. are identical with, or consist for the most part of, sitosterol. It should, however, be pointed out that *Wagner and Clement* showed that the unsaponifiable matter of cottonseed oil (Vol. II. "Cottonseed Oil") contains two " phytosterols " of the melting point 139° and 132°-133° C. respectively. The " phytosterol " obtained from *Echinophora spinosa*, L.,[6] appears also to be identical with sitosterol.[7]

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[1] It may be pointed out that *Menozzi* ascribes the same (erroneous) composition, viz. $C_{26}H_{44}O.H_2O$ to bile (egg yolk) cholesterol. See p. 265, footnote 4.

[2] *Atti R. Accad. dei Lincei*, 1908, i. p. 95; 126; *ibid.*, 1901, i. 127.

[3] O. Schreiner and E. C. Shorey, *Journ. of Biolog. Chem.*, 1911 (ix.), 9. Another alcohol, differing from phytosterol, also melting at 135° C. and giving the "cholestol" reaction, has also been found in the soil by Schreiner and Shorey, *Journ. Amer. Chem. Soc.*, 1908, 1295; 1909, 116. This alcohol is named by these authors "Agrosterol" and occurs in the free state.

[4] *Liebig's Annal.* 122. 249; 127. 105.

[5] *Journ. f. prakt. Chem.* 90, 328.

[6] *Ibid.*, 1863, 544.

[7] *Liebig's Annal.* 192. 175.

The most prominent characteristics of a number of these various alcohols have been recorded by *Gérard*,[8] *Burian*,[9] *Ritter*,[10] *Hauth*,[11] *Klobb and Bloch*,[12] *Welsch*,[13] *Cohen*, *Power* and his collaborators, and *Klobb*.[14]

In the commercial preparation of vegetable oils and fats the latter dissolve small quantities of " phytosterol " forming a very characteristic concomitant of all vegetable oils and fats (difference from animal oils and fats). The proportion of " phytosterol " in vegetable oils and fats is somewhat larger than that of cholesterol in animal oils and fats.

Sitosterol in many respects resembles cholesterol; it differs, however, from it in its crystalline form, melting point, magnitude of optical rotation, melting point of the esters (notably so of the acetate), and chemical constitution. The " phytosterol," isolated by *Bömer* from a number of commercial oils and fats, crystallises in solid needles, grouped in tufts; under the microscope there are discerned long, solid needles arranged in star- or bunch-like groups (cp. Illustrations in Chap. IX.). These crystals belong most likely to the monoclinic system, and have the composition expressed by the formula $C_{27}H_{46}O + H_2O$; they melt at 137°-138° C. (*Bömer*), 138°-143·8° C. (corr.), according to the purity of the preparation. A carefully purified specimen of sitosterol from cottonseed oil melted at 139° C. (*Matthes and Heintz* [1]).

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[1] Schulze and Barbieri, *Journ. f. prakt. Chem.* 25, 160; Frankforter and Harding, *Journ. Amer. Chem. Ind.*, 1899, 758.

[2] Tauret, *Compt. rend.*, 1889 (108), 98; *Ann. de Chim. et de Phys.*, 1908 (8), 15, 313; Gérard, *Compt. rend.*, 1892 (114), 1544; Ottolenghi, *Chem. Centrabl.*, 1906 (i.), 541; Zellner, *Monatsh. f. Chem.* (26), 727; (29) 45, 1171.

[3] Hydrocarotol mentioned in the 4th edition of this work is a hydrocarbon (Willstätter, *Liebig's Annal.* 355, 1).

[4] Welsch, *Inaug. Dissert.*, Offenbach a/M., 1909.

[5] *Berichte*, 1906, 4379.

[6] Tarbouriech and Hardy, *Bull. d. Scienc. Pharmacol.*, 1907, 387.

[7] A phytosterol, having the composition $C_{20}H_{34}O$, and melting at 135°-136° C., was found by Power and Salway, *Pharm. Journ.*, 1907 (79), 126, in the fat from *Brucea antidysenterica*, Lam.

[8] *Compt. rend.*, 1892 (114), 1544.

[9] *Monatsh. f. Chem.*, 1897 (18), 561.

[10] *Zeits. f. physiol. Chem.* 34, 461.

[11] *Inaug. Dissert.*, Freiburg i/B., 1907.

[12] Bloch, *Bull. Scienc. Pharmacolog.* 17, 160; *Compt. rend.*, 1909 (149), 999. The following alcohols may be mentioned briefly:—Betasterol (*Berichte*, 1903, 975); Arnisterol, m.p. 249°-250° C. (*Compt. rend.*, 1905 (140), 1700); Sojasterol (*Bull. Soc. Chim.*, 1907, 1. 422); cp., however, Vol. II. Chap. XIV. "Soya Bean Oil." For "phytosterols" from Balata, African rubber, and for "lupeol" (which may be identical with "arnisterol"), cp. N. H. Cohen (above, p. 273). For *a*-"phytosterol" $C_{20}H_{34}O$, melting at 134°-135° C., from nutmeg butter, cp. Power and Salway, *Journ. Chem. Soc.*, 1907, 2037. Faradiol is a dihydric alcohol $C_{30}H_{50}O_2$.

[13] *Inaug. Dissert.*, Offenbach a/M., 1909.

[14] *Bull. d. Scienc. Pharmacol.*, 1910 (xvii.), March, April, and May.

The alcohol first described as sitosterol was found by *Burian* [2] in the "unsaponifiable matter" of the oils from wheat and other germs of the gramineæ. Hence, the "cholesterol" stated by *Hoppe-Seyler and Hopkins* to occur in maize oil is most likely sitosterol.[3] It crystallises in white laminæ of silky lustre, simulating the appearance of gall cholesterol. From dilute alcohol, sitosterol crystallises with one molecule of water; hence the formula $C_{27}H_{46}O + H_2O$ was assigned to it. From ether it crystallises in anhydrous needles. Sitosterol melts at 137·5° C. (*Burian*), 136·5° C. (*Ritter*). It is easily soluble in ether, chloroform, benzene, carbon bisulphide, and hot alcohol, but sparingly soluble in cold alcohol. It is much less soluble in cold petroleum ether than is cholesterol; 150 c.c. of petroleum ether boiling below 50° C. dissolve 0·039 to 0·044 grm.; 10 c.c. of absolute alcohol dissolve 0·173 grm. (*Polenske*). $[a]_D = -26{\cdot}71°$.[4] $[a]_D^{15} = -23{\cdot}14°$ (*Matthes and Heintz* [5]).

Sitosterol carefully distilled *in vacuo* passes over unchanged, and retains its lævo-rotation; when distilled rapidly under ordinary pressure, strongly dextro-rotatory distillation products result. *Engler* obtained from "phytosterol" [6] four fractions which in 10 per cent chloroform solution gave in a 200 mm. tube the following saccharimeter "degrees":— ± 0; + 13·0; + 16·0; + 12·0 respectively.

In the *Liebermann-Burchard* "cholestol" test, as also in the *Salkowski* reaction, sitosterol behaves like cholesterol.

With metallic sodium in amyl-alcoholic solution sitosterol yields *dihydrophytosterol*, $C_{27}H_{48}O$, melting at 175° C. (*Hauth*). This characteristic derivative of phytosterol may be used for purposes of identification. Dihydrophytosterol was obtained from the phytosterol of linseed oil, as also from *Burian's* sitosterol. It still contains one pair of doubly-linked carbon atoms; hence it must be concluded that phytosterol contains at least two pairs of unsaturated carbon atoms.

Sitosterol yields with bromine a dibromo-derivative,[7] soluble in a mixture of ether and glacial acetic acid (difference from cholesterol dibromide) and crystallising only with difficulty. On adding water to its solution in ether and glacial acetic acid, it is thrown down as a heavy oil, which can only be obtained with very great difficulty in a crystalline state.

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[1] *Arch. d. Pharm.*, 1909 (247), 161.

[2] *Monatsh. f. Chem.*, 1897 (18), 561.

[3] A. H. Gill and C. G. Tufts, *Journ. Amer. Chem. Soc.*, 1903, 25, 251.

[4] *Zeits. f. physiol. Chem.* 34, 431.

[5] Pickard and Yates (*Journ. Chem. Soc.*, 1908, 1930) found for a specimen of sitosterol from wheat germs, after heating it to 100° C.:—$[\alpha]_D$ (in chloroform) $= -34{\cdot}4$ ($c = 5{\cdot}5$) and $[\alpha]_D$ (in ether) $= -23{\cdot}21$ ($c = 2{\cdot}9$).

[6] The phytosterol is described as having been bought from Merck. Most probably this is a phytosterol obtained from Calabar beans; but as the melting point has not been stated, it must be left open to doubt whether all stigmasterol had been removed.

[7] Windaus, *Chem. Zeit.*, 1906, 1011.

With *Hübl's* solution phytosterol gives an iodochloro compound; the iodine value of phytosterol was found by *Matthes and Heintz*,[1] 62·79 (theory 65·8). With *Wijs'* iodine solution erratic results are obtained (cp. Chap. VIII.).

Sitosterol absorbs 24·85 per cent of ozone, whereas theory requires for 2 molecules of ozone an increase of 24·84 per cent (*Molinari and Fenaroli*). The oxidation products of phytosterol are being studied by *Pickard and Yates*.[2]

Esters of Sitosterol

Sitosteryl formate, $C_{27}H_{45}O.CHO$, melts at 105·5°-114·3° C. (corr.), according to the purity of the various preparations of " phytosterol " obtained from different oils (*Bömer*). The crystals closely resemble those of " phytosterol " itself.

Sitosteryl acetate, $C_{27}H_{45}O.C_2H_3O$, crystallises, from a concentrated solution, in bunches of very fine needles; from a very dilute solution, plates resembling " phytosterol " itself were frequently obtained. The melting point of the acetate is 125·6°-137° C. (corr.) (*Bömer*), according to the purity of the preparations obtained from the different oils. Acetates prepared by other observers from cottonseed oil " phytosterol " melted at 125° C. (*Wagner and Clement*), 123·5° (*Matthes and Heintz*); from dadap seed fat phytosterol at 130° (*Cohen*). The melting point of a pure acetate obtained from *Burian's* sitosterol, as also from Calabar beans, was found by *Hauth*, 127° C. $[\alpha]_D^{15} = -21{\cdot}42^\circ$ (*Matthes and Heintz*).

The dibromide melts at 135° C. (*Rohdich*), 127° (*Heiduschka and Gloth*[3]).

Sitosteryl propionate, $C_{27}H_{45}O.C_3H_5O$. The crystals are mostly obtained as very fine needles; occasionally they form large plates very similar to those which " phytosterol " itself exhibits. The melting point varies from 106° to 117·3° C., according to the purity of the preparations obtained from the various oils. The melting point of propionate from *Burian's* sitosterol is 108·5° C.

Sitosteryl (normal) *butyrate*, $C_{27}H_{45}O.C_4H_7O$, crystallises in forms very similar to those of " phytosterol " itself. The crystals melt at 68·5°-90·6° C. (corr.), according to the purity of the preparations obtained.

Sitosteryl benzoate, $C_{27}H_{45}O.C_7H_5O$, crystallises in rectangular plates very similar to those of cholesteryl benzoate. Preparations obtained from cottonseed oil and sesamé oil "phytosterols," melted at 145·3°-148·4° C. (corr.). The benzoate obtained from *Burian's* sitosterol melts at 145°-145·5° C. (*Ritter*[4]).

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[1] *Arch. d. Pharm.*, 1909 (247), 161.

[2] *Proc. Chem. Soc.*, 1908, 227; *Journ. Chem. Soc.*, 1908, 1928.

[3] *Pharm. Zentralh.*, 1908 (49), 836.

[4] For other esters, and the several liquid phases which "phytosteryl" esters exhibit, cp. Jäger, *Rec. d. trav. chim. Pays-Bas*, 1906, 334; *Proceed. K. Akad. van Wetensch.*, Amsterdam, 1907, 483; Wallerant, *Compt. rend.*, 1906 (143), 605.

(2) BRASSICASTEROL, $C_{28}H_{46}O + H_2O$

Brassicasterol occurs in rape oil (*Windaus and Welsch*[1]). It has been prepared from its pure acetate in the form of hexagonal leaflets, melting at 148° C. In chloroform solution the specific rotation is $[\alpha]_D^{18} = -64° 25'$, in ethereal solution $[\alpha]_D^{18} = -63° 31'$.

Brassicasteryl acetate, $C_{28}H_{45}O.C_2H_3O$, obtained by reduction of its tetrabromo-derivative, crystallises in thin hexagonal leaflets, melting at 157°-158° C. The *tetrabromide*, $C_{30}H_{48}O_2Br_4$, crystallises in rhombic plates; it is sparingly soluble in methyl alcohol, ethyl alcohol, and glacial acetic acid, more readily soluble in acetone and ether, very easily soluble in chloroform. It decomposes at 209° C.

Brassicasteryl propionate, $C_{28}H_{45}O.C_3H_5O$, prepared by heating brassicasterol with propionic anhydride, crystallises from alcohol in thin quadrangular leaflets, melting at 132° C. The *tetrabromide* forms rhombic plates melting, with decomposition, at 206° C. On reduction with zinc dust and glacial acetic acid the propionate is re-formed.

Brassicasteryl benzoate, $C_{28}H_{45}O.C_7H_5O$, obtained by heating brassicasterol with benzoyl chloride, melts at 167° C. to form a turbid liquid, which becomes clear at 169°-170° C.

(3) STIGMASTEROL, $C_{30}H_{48}O$ (or $C_{30}H_{50}O$) + H_2O

Stigmasterol was first found in Calabar bean "phytosterol,"[2] of which it constitutes 20 per cent. This alcohol has also been found to occur, mixed with ordinary "phytosterol," in a number of oils and fats (see Vol. II. Chap. XIV.). Very likely this alcohol occurs frequently in admixture with sitosterol in the unsaponifiable matter of vegetable oils and fats. This would explain the great difference in the melting points of the esters of "phytosterol" found by *Bömer* (see above). The alcohol forms crystals melting at 170° C., and appearing under the microscope, to be practically identical with those of "phytosterol." In the *Liebermann-Burchard* "cholestol" reaction, stigmasterol behaves exactly like "phytosterol." In chloroform solution the specific rotation is $[\alpha]_D^{21} = -45{\cdot}01°$; in ethereal solution $[\alpha]_D^{24} = -44{\cdot}67°$.

This alcohol contains two pairs of doubly-linked carbon atoms, as it yields a tetrabromo-derivative, $C_{30}H_{48}OBr_4$.

Stigmasteryl acetate, $C_{30}H_{47}O.C_2H_3O$, obtained by reduction of its tetrabromo-derivative, crystallises in rectangular plates; it is easily soluble in acetone, chloroform, ether, sparingly soluble in methyl and ethyl alcohols, and melts at 141° C. The *tetrabromide*, $C_{30}H_{47}O.C_2H_3O.Br_4$, is sparingly soluble in methyl alcohol, ethyl alcohol, and glacial acetic acid, easily soluble in hot benzene, and with difficulty soluble in ether and acetone. It melts at 211°-212° C.

Stigmasteryl propionate, $C_{30}H_{47}O.C_3H_5O$, crystallises from alcohol in prisms melting at 122° C. The tetrabromo-derivative melts, with decomposition, at 202° C.

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[1] *Berichte*, 1909, 612.

[2] Windaus and Hauth, *Berichte*, 1906, 4378. *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 267.

Stigmasteryl benzoate, $C_{30}H_{47}O.C_7H_5O$, crystallises in quadrangular plates melting at 160° C.

COPROSTEROL, $C_{25}H_{44}O(C_{27}H_{46}O\ ?)$[1]

This alcohol is formed through the reduction of cholesterol (which is discharged with the bile) by the bacteria occurring in the intestines. Hence it occurs in considerable quantities in sewage fats (see Vol. III. Chap. XVI.). *König and Schluckebier* found it also in considerable quantities in the excrements from animals fed with peas, maize, cocoanut cake, and sesamé cake. It would therefore appear that "phytosterol" also is reduced to coprosterol in the alimentary canal.[2]

Coprosterol crystallises from 85 per cent alcohol in long fine needles, melting at 95°-96° C.; 99°-100° C. (*Dorée*). It dissolves easily in absolute alcohol, chloroform, ether, carbon bisulphide, benzene, and petroleum ether. It rotates the plane of polarisation to the right; $[\alpha]_D^{20} = +24°$. It differs from cholesterol by its crystalline form, its melting point, the sense and magnitude of the optical rotation, and the melting point of its benzoate. On treatment with ozone, coprosterol absorbs one molecule of ozone (*Dorée* [3]).

By the action of sodium amyloxide on coprosterol, an isomeric coprosterol is obtained (*Dorée*).

Coprosteryl acetate crystallises from a mixture of alcohol and ether in rectangular plates melting at 114°-115° C. According to *Dorée* [4] the acetate crystallises in needles melting at 88° C.

The separation of coprosterol from cholesterol and sitosterol, if occurring together (as in the case of sewage fats), is effected by 80-85 per cent alcohol.

Coprosteryl benzoate, crystallises in plates, melting at 122° C. (*Dorée*).

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[1] Cp. C. Dorée and J. A. Gardiner, *Journ. Chem. Soc.*, 1908, 1625.

[2] Cp., however, Levites, *Hoppe-Seyler's Zeits. f. physiol. Chem.*, 1908 (57), 46. Cp. also C. Kusumoto, *Biochem. Zeits.*, 1908 (14), 407, 411, 416.

[3] *Journ. Chem. Soc.*, 1909, 646.

[4] *Biochem. Journ.*, 1909 (4), 79.

CHAPTER IV

PREPARATION OF THE FATTY MATTER FOR EXAMINATION —PRELIMINARY TESTS

THE commercial preparation of the raw materials used in the oil and fat industries, and the methods of refining and bleaching them, will be discussed in the second volume of this work (see Chap. XIII.). In this section we deal with the fatty materials as they reach the works' yard or the chemical laboratory. Preparatory to the analytical examination by physical and chemical methods, the fatty matter must be freed from foreign substances.

Sampling

In sampling a cask or barrel of fat one must be careful to obtain a sample which shall actually represent the bulk. This can easily be done in the case of oils (liquid fats), and all that is necessary is to stir thoroughly any separated " stearine " (*e.g.* cottonseed oil) into the bulk of the oil. In the case, however, of solid fats special caution must be observed, or grave errors may be committed.

The following reliable method of sampling tallow and other solid fats is the one used at seaports and in works. By means of an auger a cylindrical sample of fat, at least eight inches long and one inch thick, is taken from each cask, or a convenient number of casks, and each sample is labelled with the number and marks of the cask, the gross weight and tare of each cask being also noted. If there be reason to presume the admixture of gross impurities such as sand, etc., which collect at the bottom of the cask or barrel, then it is advisable to take further samples by boring a hole on the opposite side of the bung-hole of the cask or barrel. It may even be necessary to bore holes for sampling purposes through the ends of the packages, or in extreme cases to take off one end of the cask or barrel and draw a number of samples by inserting the auger in different places and at different angles.

The several samples are mixed in the laboratory in quantities proportionate to the net weight of their respective casks, and the mass thus obtained is melted on the water-bath in a dish, at a temperature not exceeding 60° C., with constant stirring As soon as the fat is melted, the dish is removed from the water-bath and the mass is stirred vigorously in order to prevent water and impurities from settling down to the bottom of the dish.

The first operation in the examination of fats is the estimation of water and of those substances of a non-fatty nature which can be readily separated from the fat. It should be borne in mind that a number of bodies, such as rosin, paraffin wax, paraffin oils, tar oils, and rosin oils, remain dissolved in the fat. These substances, excepting rosin, are comprised under the term "unsaponifiable matter." Their determination, as also that of rosin, is carried out when the examination of the dry and preliminarily purified fat is reached.

Estimation of Water

About 5 grms. of the sample are weighed accurately in a small beaker or wide-mouthed flask containing a thin glass rod, and dried at 100°-110° C. until the weight remains constant, or, at any rate, until the loss after drying for one hour does not exceed 1 or 2 mgrms. (cp. Chap. VIII.). The drying should not be pushed beyond a point when approximately concordant results have been obtained; as a rule, this will be reached within a few hours. Otherwise, slight loss may be caused by volatilisation of lower fatty acids (contained originally in the substance, or formed by hydrolysis at the high temperature) or an increase of weight may take place owing to absorption of oxygen. It should be noted that both volatilisation and consequent decrease of weight on the one hand, and oxidation and consequent increase of weight on the other hand, may take place simultaneously, so that these two sources of error may to some extent balance one another (cp. also Chap. VIII.).

Whilst drying, it is advisable to stir the fat from time to time, as water will collect below the fat, and only slowly evaporate through it. This method will be found suitable in the case of solid and not readily oxidisable fats. In the case of drying oils, it is advisable to dry in a current of carbon dioxide, or coal gas, or hydrogen. The oil is then best weighed in a flask closed by a cork perforated with two holes, through one of which a straight tube passes to the bottom of the flask, whilst the other is fitted with a bent tube ending with the cork. A calcium chloride tube is then attached to the straight tube, the bent tube is connected with the filter pump, and a current of gas is drawn through the oil at 100° C.[1]

In case the fats contain water in persistent emulsion it may be found expedient to admix dehydrated sodium sulphate with the sample.[2] Better still is to treat such a sample in an extractor (see below).

For the determination of water in butter fat and margarine, dried sand is mixed with the sample; cp. Vol. II. Chap. XIV. "Butter Fat"; for the determination of water in bone fat and in tallow see Vol. II. Chap. XIV. "Bone Fat" and "Beef Tallow"; in lubricants see Vol. III. Chap. XV. "Lubricating Oils—Lubricants"; and in Dégras see Vol. III. Chap. XVI. "Sod Oil—Dégras."

In case caustic potash, or potash soap, or lime soap have been fraudulently added to tallow, etc. (in order to facilitate the incorporation of water), the fat cannot be freed from the last traces of water by drying at 100° C. Bone fats normally retain lime soaps which do not readily part with the contained moisture even at 130° C. The safest plan in these cases is to determine the amounts of fatty matter, impurities, and of potash or lime separately, and to take the percentage of water by difference (cp. " Bone Fat," Vol. II. Chap. XIV.).

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[1] Cp. *Journ. Soc. Chem. Ind.*, 1886, 508 (Illustration).

[2] Cp. G. Perrier, *Ann. chim. anal. appl.*, 1909 (14), 367.

Very small quantities of water—below 0·5 per cent—in lard can be ascertained with great accuracy by determining the temperature at which the melted lard becomes turbid (cp. Vol. II. Chap. XIV. " Lard "). This method is, however, not applicable to the determination of moisture in tallow.[1]

For the determination of water by distillation after addition of toluene or xylene cp. Vol. III. Chap. XV. " Lubricating Oils " ; cp. also *F. Michel*.[2]

Determination of Foreign Substances

To determine solid substances, such as remnants of vegetable or animal tissue, dirt, or fraudulent admixtures, 10-20 grms. of dried[3] fat are extracted in a flask by shaking with one of the following solvents : petroleum ether, ether, chloroform, carbon tetrachloride,[4] trichlorethylene, or benzene. Carbon bisulphide which is largely used in French laboratories is best avoided. The solution is then poured through a tared filter and the residue washed on the filter with the same solvent, until a few drops of the filtrate, evaporated on paper, no longer leave a grease-spot. The filter with its contents is then dried at 100° C. and weighed. The dried residue may be incinerated and weighed again, when the difference will give the amount of organic matter. If the amount of ash is large (salt, chalk, clay, or lime from fraudulently added lime soap), further examination of these foreign matters is required.

Of the foregoing solvents, petroleum ether will be found the most convenient, inasmuch as it dissolves smaller quantities of resinous bodies than do any of the other solvents mentioned. Therefore, if there be no reason against the use of petroleum ether—*e.g.* in the case of castor oil[5]—this solvent should be employed ; all the more so, as it can easily be obtained in a state of purity and free from acid ; besides, it need not be dried beforehand. It should, however, be rectified carefully by means of a fractionating column, and all portions boiling above 80° C., or in some cases above 50° C., should be discarded. If necessary, it should be purified by shaking with a little concentrated sulphuric acid ; after separation from the dark acid layer, the petroleum ether must be washed with water until entirely free from acid ; it is best to distil it off, so as to free it from any remaining high boiling substances, formed by the treatment with sulphuric acid.

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[1] Fischer and Schellens, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xvi. 161.

[2] *Chem. Zeit.*, 1913, 353.

[3] With regard to " Bone Fats " cp. Vol. II. Chap. XIV.

[4] Cp. O. Rammstedt, *Chem. Zeit.*, 1909, 94.

[5] Sulphur olive oil oxidised acids ; dégras oxidised acids also require special consideration ; see Vol. II. "Sulphur Olive Oil." Cp. p. 285.

In the case of bone fats, *Shukoff and Schestakoff*[1] showed that the choice of the solvent is not immaterial, as carbon bisulphide indicates less insoluble matter than does petroleum ether; carbon bisulphide also extracts more lime soap in the hot than in the cold. Thus a sample of bone fat treated with hot carbon bisulphide and filtered rapidly gave 1·1 per cent of insoluble matter, whereas after cooling 6·5 per cent were obtained.

If a considerable quantity of organic matter has remained on the filter, the residue should be tested for soaps of the alkaline earths, metallic soaps (aluminium soaps, etc.), and starch. On treating the residue with mineral acids, the soaps are decomposed with liberation of fatty acids which remain on the filter, whilst the metals pass into the aqueous solution.

Starch can be detected in the organic residue by the blue colouration it gives with iodine solution; its presence is confirmed by microscopical examination. It is important to note that on dissolving a fat in petroleum ether, etc., starchy matter is liable to retain some fat. Hence the amount of starch found does not coincide exactly with the weight of the dried residue. *König* recommends, therefore (especially in butter analysis), to wash the residue, after exhaustion with ether, with cold water, in order to remove any water-soluble substances. The residue is rendered soluble by boiling with water, and is finally converted into glucose by heating with hydrochloric acid. The glucose may be estimated by means of *Fehling's* solution.

Ethereal oils contained in some natural fats, as in nutmeg butter, are best determined by distillation in a current of steam. On weighing the remaining dried fat, the quantity of essential oil will be found by difference. The distillate may be shaken out with ether, and the ether residue further examined.

Naphtha in extracted greases (see Vol. III. Chap. XVI.) may be determined in the same manner, viz. by passing a current of steam through 50 or 100 grms. of the sample. Large quantities are best determined as described in Chapter VI. "Unsaponifiable Matter."

Substances **soluble in water** (some, *e.g.* common salt, may be found on the filter) are removed from the fat by shaking a large quantity, about 50-100 grms., with warm water, so as to melt the fat. The mixture is allowed to stand in a warm place until it has separated completely into two layers. Should the separation not be complete after a short time, or should part of the fat form an emulsion with the aqueous layer, addition of a little ether will be found effective in causing separation. The aqueous liquid is then removed by means of a separating funnel and examined. Any existing traces of sulphuric acid (left in the oil from refining operations) will be found in this aqueous layer, and are estimated by titration with standard alkali, using methyl-orange as indicator. Other substances present may be determined in the residue left on evaporation.

At the seventh International Congress of Applied Chemistry,

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[1] *Journ. Soc. Chem. Ind.*, 1898, 805. *Chem. Revue*, 1898, 6.

London, 1909, ***Frank Tate*** submitted the following description of the methods adopted in his laboratory for the estimation of impurities in the most frequently occurring cases :

Greases other than Naphtha Greases—Water.—50 grms. are heated in a crucible on asbestos felt, or a sand-bath, over a low Bunsen flame, until all the signs of ebullition have ceased, and the fat is in a condition of calm fusion, without giving off vapour. Allow to cool and weigh; the loss multiplied by two gives the percentage of water in the sample.

Total Naphtha—if Naphtha be present.—50 grms. of the sample are placed in a flask, and steam is passed into the flask. The naphtha and steam passing off are condensed in an ordinary condenser, and the whole collected in a graduated tube. The naphtha floats on the top of the condensed water, its volume is noted when the amount is constant, and the weight calculated from its specific gravity.

The water in the presence of naphtha is estimated by heating 50 grms. of the sample in a crucible on a sand-bath, or asbestos, as described above. The loss gives the amount of water in the sample and some, or all, of the naphtha. The grease is now removed to a flask and distilled with steam, and any naphtha in the grease is condensed and measured, and its weight calculated from the specific gravity.

The amount of naphtha obtained by this distillation deducted from that obtained by the distillation for total naphtha gives the amount of naphtha which passed off with the water when the 50 grms. of the sample were heated in the crucible on the sand-bath ; this amount deducted from the total loss gives the water only.

Lime-soap, etc.—10 grms. of the sample (undried) are treated with petroleum spirit (of 0·700 sp. gr.) at a temperature of from 15·5° C. to 20° C. (not higher). The insoluble residue is collected on a tared filter paper and washed with petroleum spirit at the above temperature ; the last washings are tested by evaporation for presence or absence of fat, and the filter paper and insoluble residue is dried at 212° Fahr. and weighed ; the result gives the "*lime-soap*" and the "*dirt.*" After weighing, the residue is treated with dilute hydrochloric acid to decompose the soap ; the fatty acids from the soap are collected, weighed, and calculated to the equivalent fatty anhydrides in the usual way.

The remainder represents the "*Mineral and other matters free from fat.*"

It is advisable to ensure that none of the lime-soap has been dissolved by the petroleum spirit at the temperature employed. This may be done by estimating the lime in the solution resulting from the treatment of the "lime soap and dirt" with hydrochloric acid after removal of the fatty acids as above directed. The amount of lime so obtained should agree with the lime ascertained by igniting 10 grms. of the fat and estimating the lime in the resulting ash.

Determination of Fat in the Sample

The determination of true fat in a sample is conveniently combined with the estimation of foreign substances (see above) by collecting the filtrate in a tared flask, evaporating the solvent, and weighing the dried residue.

If mucilaginous, starchy, or other solid substances are intermixed with the fat, the following process will be found more convenient and more reliable. The sample is intimately mixed with 4-6 times its weight of sand or, if water is retained tenaciously, finely powdered gypsum (previously washed and heated), and dried at 100° C. The mass is then transferred to an automatic extractor.

The most convenient apparatus for the extraction of fat is the one devised by *Soxhlet* (*Szombathy*) (Fig. 1). A modification of this apparatus, which is frequently preferred, being less liable to break, is shown in Fig. 2.

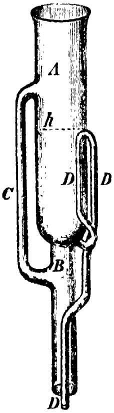

Fig. 1.

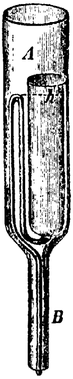

Fig. 2.

The substance to be extracted is placed in a cartridge of filter paper, prepared by rolling filter paper round a cylindrical piece of wood of suitable size and folding it up at one end. The cartridge is filled with the substance and transferred to the extractor A. Care must be taken that the syphon tube be not stopped up by the paper case; nor should the cartridge be filled to the top, lest some particles of the substance be washed over by the solvent and carried away. To be quite safe, it will be found advisable to place a plug of (extracted) cotton-wool on the top of the substance, or to close the top by folding the paper over it.[1] The tube B is then fitted by means of a cork to a flask charged with about 50 c.c. of the solvent (petroleum ether, ether, chloroform, etc.). Another portion of the solvent is carefully poured on to the substance in B, until it commences to run off through the syphon D. Finally an inverted condenser is fitted to A, and the whole apparatus placed on a water-bath. As the solvent boils, the vapours pass through B and C into the condenser, and fall condensed on to the substance in the paper case. When the liquid has reached the level *h*, the solution syphons off automatically through D, and A is emptied completely. The solvent is again evaporated and recondensed, and thus serves again for extracting, and so on. In this way the vessel A may easily be filled and emptied twenty to thirty times within an hour.

The choice of the solvent is by no means immaterial, and the general assumption that the selection of the solvent may be allowed to depend on the convenience of the operator must be considered erroneous. It is frequently found that one specific solvent does not extract the fat completely from every fat-containing substance. This is especially noteworthy in the case of products of the animal organism such as meat, egg yolk, etc. (cp. Vol. II. Chap. XIV. "Egg Oil"; also *Kumagawa and Suto* [1]), and in the case of the fatty matter contained in the heart, liver, etc. Large amounts of lecithin (phosphatides) in these organs prevent on the one hand complete extraction with ether, on the other hand the ether extracts, in addition to fats, also other substances.[2]

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[1] H. Bull and H. Gregg (*Tidskrift for Kemi*, 1912, 321) state that in the extraction of whale meal (also of cotton), etc., the ether passes through the filter paper in preference to percolating the substance. They therefore recommend to fix inside the cartridge of the filter paper a cylinder of sized writing paper.

As a general rule, it may be stated that ether, carbon bisulphide, and carbon tetrachloride [3] dissolve all fatty substances present with equal facility. If strictly accurate results be required, it is always advisable to treat the extracted meal, etc., with petroleum ether. (Cp. also Vol. II. Chap. XIII.) Thus petroleum ether does not dissolve the oxidised acids of, *e.g.*, sulphur olive oil, dégras, etc. (cp. "Sulphur Olive Oil"); nor does it dissolve theobromine from cacao beans, whereas ether readily extracts this alkaloid together with the cacao butter. In other cases, as in dressings of textile fibres, stannic chloride is readily extracted both by dry ether and petroleum ether. Also aluminium, ferric, and stannous chlorides are dissolved by ether. Hence it is necessary to extract textile goods with water previous to extracting fatty substances. For the determination of fat in foodstuffs cp. *E. Polenske*.[4]

When using the form of *Soxhlet's* extractor described above, there is always some doubt as to the exact time when the extraction is complete, and, as a rule, the operation lasts much longer than necessary, involving both loss of time and of solvent. To avoid this *Lewkowitsch* [5] has a tap fitted on to the syphon tube, so that some of the solvent can be withdrawn at any time to ascertain the progress of extraction (Fig. 3).

Fig. 3.

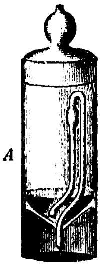

Fig. 4.

If the substance to be exhausted has been collected on a filter, the simplest plan is to fold the filter over the substance and place it at once in the extractor.

Frühling [6] proposed a modified form of the *Soxhlet* extractor which admits of convenient handling for weighing before and after the extraction. The essential part of the apparatus, which serves for the reception of the sample, is shown in Fig. 4. It has the form of an ordinary filter-weighing bottle, differing only from it in that the bottom has a funnel-like shape. It is provided with a syphon, the longer limb of which passes through the bottom, where it is cut off aslant. The sides of A are continued beyond the protruding limb of the syphon, so as to allow of its standing in an upright position on the pan of a balance ; at the same time the tube is thus protected from breakage. The shorter limb of the syphon reaches to the bottom of the bottle, and in its upper part is provided with a bulb which serves to sever the column of the solvent when the bottle is taken out of the tube B (Fig. 5). This tube is the ordinary form of the *Soxhlet* extractor without its syphon tube, and serves for the reception of A. The upper part of B may be fitted with a carefully-ground stopper, to which is attached tube C. The whole arrangement and application of the apparatus will be readily understood from a glance at the annexed figures.

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[1] *Biochem. Zeits.*, 1908 (8), 212; cp. Shimidzu, *ibid.*, 1910 (10), 237; Koch, *Chem. Zeit.*, 1911, 1040.

[2] Hartley, *Journ. of Physiol.*, 1907 (36), 17; E. Schulze, *Zeit. f. angew. Chem.*, 1908, 1125; Fahrion, *ibid.*, 1909, 769.

[3] Cp. E. P. Harding and L. L. Nye, *Journ. Ind. Eng. Chem.*, 1912, 895. In the extraction of fæces carbon tetrachloride extracts in twelve hours 17·9-33·8 per cent more of fatty matter than does dry ether in 24 hours (A. D. Emmett, *Journ. Amer. Chem. Soc.*, 1909 (31), 693). Cp. also Chapus, "Analyse et dosage des matières grasses dans les fèces," *Journ. de Pharm. et de Chim.*, 1909, 301.

[4] *Arb. a. d. Kais. Gesundheitsamte*, 1910 (xxxiii.), 563.

[5] *Journ. Chem. Soc.*, 1889, 360.

[6] *Journ. Soc. Chem. Ind.*, 1889, 568.

For the extraction of substances at the boiling point of the solvent, *F. K. Stock* recommended a suitably modified extractor.[1]

The number of modifications and improvements of *Soxhlet's* ingenious apparatus is almost legion. As the above-described forms will be found suitable for most purposes, the reader must be referred for further information to the pages of the *Journal of the Society of Chemical Industry*, where a complete record of all proposed forms will be found.

When the extraction is complete, the flask containing the solution is detached from the extractor, the solvent distilled off on the water-bath, and the fat dried in an air-bath at a temperature not exceeding 100°-110° C., until the weight remains fairly constant (cp. Chap. VIII.).

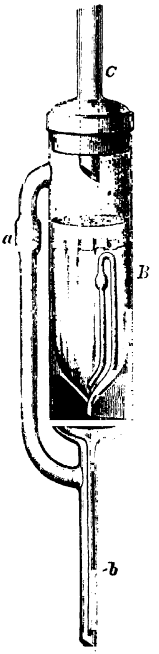

Fig. 5.

The apparatus described above will also be found useful for the estimation of the fat contained in oleaginous seeds, oil-cakes, etc. Previous to the extraction, the substances must be disintegrated to a fine powder, and, if required, dried at a suitable temperature (cp. Vol. II. Chap. XIII.).

The drying and filtering of the fat is best carried out in a spacious drying oven provided with a thermostat (thermo-regulator).

The drying oven may be one of the customary type of about the following dimensions : 10 inches high, 10 inches broad, and 6 inches deep. An apparatus the author had made with slight alterations after *Sidersky's*[2] design, consists of a jacketed cylindrical oven provided with a door having a thick glass plate and closing hermetically. Suitable taps allow the drying to proceed *in vacuo* or in a current of dried air or of an indifferent gas, which can be aspirated slowly through the drying chamber. The space between the two cylinders may be filled with water or any other suitable liquid; thus the desired temperature can be kept constant without attention for any length of time.

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[1] *Journ. Soc. Chem. Ind.*, 1897, 107 ; cp. also E. B. Warren, *Analyst*, 1906, 314.

[2] *Ibid.*, 1890, 967.

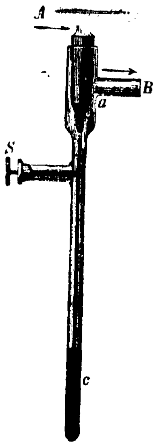

Fig. 6.
½ actual size.

Reichert's improved form of thermo-regulator[1] is shown in Fig. 6. It consists of a capillary tube enlarged at the bottom to a bulb *c*,—in short, a thermometer, the top part of which is widened out as shown. The capillary branch tube is supplied with a screw S, by means of which the level of the mercury may be adjusted at will. The gas-supply tube A is carefully ground into the upper part of the thermometer tube, and extends down to the joint of the stem. A has an opening at the bottom, and is also perforated with a small hole at *a*. The gas entering at A leaves the regulator at B. The thermostat is fixed, side by side with an ordinary thermometer, by means of a cork perforated with two holes, into a nozzle of the drying oven; A is then connected with the gas-supply, and B with the gas-burner. The tube A must be adjusted in such a way that communication with B is established through *a*, whilst S is screwed out of the tube sufficiently far to allow the mercury to fall below the tapered part. The oven is then heated, and at the moment the desired temperature has been reached, S is screwed into the tube until the column of mercury just reaches the tube A. The exact moment is easily observed as the flame of the burner becomes smaller. Gas is then supplied to the burner through *a* only, until, in consequence of the falling of the temperature in the oven, the mercury falls, thereby allowing an additional supply of gas to flow through the lower end of A, which had been closed before by the mercury. With the rise of temperature the mercury expands, and again closes the lower opening of A, thus causing the temperature to fall, and so on. It is thus possible to keep the temperature constant within very narrow limits. In the case of the flame of the burner being too high for the desired temperature, even when gas passes through *a* only, the gas-supply must be diminished by slightly turning the tube A, thus partially closing the opening *a*.

The screw S is usually cemented by the maker of the instrument with sealing-wax, which, however, easily melts, allowing mercury to ooze through the cork; care should therefore be taken to protect the wax from becoming overheated.[2]

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[1] Cp. also the thermo-regulator made by Kob & Co., *Chem. Zeit.*, 1910, 1152.

[2] The principle underlying Reichert's thermo-regulator, but avoiding the last-mentioned drawback, has been employed by Berlemont, cp. *Journ. Soc. Chem. Ind.*, 1895, 821. Cp. especially the improved Reichert thermo-regulator described by R. Fänder, *Chem. Zeit.*, 1913, 40.

Another objection to *Reichert's* thermostat has been pointed out by *J. W. James*,[1] namely, that after short use—a few days or weeks, depending on the purity of the gas—the upper surface of the mercury becomes coated with a black powder (mercuric sulphide), which before long impairs the delicacy of the regulator. It then becomes necessary to take the apparatus to pieces for cleaning. *James* therefore designed a thermostat, making use of *Reichert's* principle, in which the objectionable passing of the gas over the surface of the mercury is avoided. For the drawing of the instrument and instructions for use the original paper should be consulted. *E. Fontaine* [2] replaces the horizontal tube of *Reichert's* thermo-regulator (ending in screw S) by a tube bent upwards at a right angle.

Another thermostat, made entirely of metal and not containing mercury, has been described by *Porges*.[3]

In a laboratory provided with steam it is most convenient to connect the jacketed drying oven with the steam supply; a thermostat can then be dispensed with.

If it is merely a question of freeing a sample of fat from water and gross impurities for subsequent examination, the fat is best melted in a dish on the water-bath and kept in the melted state until water and dirt have settled out. The clear fat is then poured off through a dried filter, which absorbs the small quantities of moisture dissolved in the fat.

Detection and Determination of Inorganic Substances in the Fatty Matter

Oils and fats dissolve small quantities of water-soluble, as also of metallic, soaps. In "boiled" oils metallic soaps are present as a normal constituent. The presence of metals is readily ascertained by burning off a few grams of fat in a porcelain crucible; if a metal be present, a residue is obtained. As a rule the following may be expected: sodium and potassium hydrates, lime, alumina, and the oxides of iron, lead, copper, zinc, tin, and nickel (in the case of "hardened" fats).

In the presence of *alkali metals* the residue dissolves in water and the solution has an alkaline reaction to litmus paper. Sodium and potassium salts are identified by applying the methods used in the analysis of soaps (Vol. III. Chap. XV.).

If *lime* be suspected, the ash is treated with dilute hydrochloric acid. After filtering, the filtrate is tested with ammonium oxalate and ammonia. A white precipitate indicates the presence of lime. For the quantitative estimation of lime the precipitated calcium oxalate is allowed to stand in a moderately warm place for twelve hours; it is then filtered, dried, and the residue heated over the blowpipe until the weight of the calcium oxide remains constant.

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[1] *Journ. Soc. Chem. Ind.*, 1893, 225.

[2] *Ann. chim. analyt. appliq.*, 1911 (16), 52.

[3] *Zeits. f. analyt. Chem.*, 1893, 212. Cp. also T. M. Lowry, *Journ. Chem. Soc.*, 1905, 1030, and *Zeits. f. Chem. Apparatenkunde*, 1906, i. 255, 281; cp. also German patent 243,047.

The separation of other metals from an oil or fat is in most cases best effected by warming the sample in a flask on the water-bath with dilute nitric acid; the metals then pass into the acid liquid. In the case of tin, only a portion of the metal is thus extracted.[1] If tin be suspected it is advisable to fuse the sample with sodium carbonate and potassium nitrate. In other cases a somewhat large quantity of the fat may be incinerated in a platinum dish (if lead be suspected, in a porcelain crucible). The resulting ash is then dissolved in a few drops of nitric acid, and the solution diluted with water. In some cases it will be found convenient to dissolve the fat under examination in ether, and to shake the ethereal solution with acidulated water.

A portion of the acid solution obtained by any of the preceding methods is tested with sulphuretted hydrogen; the presence of lead and (or) copper, or nickel is indicated by the appearance of a black or brown precipitate or colouration.

Other portions of the solution are tested (1) with potassium ferrocyanide (brown precipitate) or with ammonia (blue colouration) for *copper*;[2] (2) with sulphuric acid (white precipitate) or with potassium chromate (yellow precipitate, soluble in potash) for *lead*. For the detection and estimation of *iron* see below. *Zinc* (taken up by oils and fats from galvanised packages) and *alumina* are detected by the well-known methods of quantitative analysis.

Copper oxide is sometimes intentionally added to oils in order to impart to them a green colour. Edible fats (such as lard), when kept in copper or lead-glazed vessels, easily take up *copper* or *lead* on turning rancid. The quantitative determination of these two metals in edible oils and fats deserves, therefore, special attention.

Quantitative Determination of Copper

Weigh off accurately 10 to 20 grms. of the fat under examination in a platinum dish and incinerate. Dissolve the ash in a few drops of nitric acid, dilute with water, and filter into a beaker. Heat the solution nearly to the boiling point, add pure caustic soda or potash, and heat again for a few minutes. Filter off the black precipitate of copper oxide, dry, ignite, and weigh.

Another method is to stir the warmed fat thoroughly with hydrochloric acid, and pour the acid liquid through a filter; the fat is then washed several times with water, and the washings are added to the main portion. Next the solution is heated whilst a current of sulphuretted hydrogen is passed through it. The precipitated cupric sulphide is filtered off, washed with water containing sulphuretted hydrogen, dried, mixed with sulphur, and heated in a porcelain crucible in a current of hydrogen. The copper is thus converted into cuprous sulphide, Cu_2S.

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[1] J. A. Emery, *Twenty-sixth Annual Report of the Bureau of Animal Industry*, 1909.

[2] The flame colour reaction for copper is useless (Vaubel, *Chem. Zeit.*, 1910, 685). J. F. Sacher has shown that *moist* fats forming carbon monoxide, owing to incomplete combustion, give a green colouration which dry fats do not exhibit. Fats containing boric acid or borates give also the green colour (*Chem. Zeit.*, 1910, 824).

Quantitative Determination of Lead

The lead is brought into solution as lead nitrate by one of the methods detailed above. Dilute sulphuric acid is then added, and the solution warmed on the water-bath until all the nitric acid has evaporated off. The remaining liquid is mixed with a little water and twice the volume of alcohol. After allowing to stand for a few hours the precipitate is filtered off, washed with dilute alcohol, dried, and ignited. The filter must, of course, be incinerated separately. The resulting lead sulphate is calculated to *lead oxide* or *lead*.

The following is a more rapid, though less accurate method :—Burn off several grms. of the fat in a tared porcelain crucible. The residue, consisting of a mixture of metallic lead and lead oxide, is weighed, and then treated with warm acetic acid to dissolve the lead oxide. The metallic lead is washed by decantation, and the crucible dried and weighed again, whereby the amount of metallic lead is found. The difference between the two last weights corresponds to the amount of lead oxide ; it is calculated to *lead*, and the quantity is added to that found for the metallic lead.

Another rapid method is to shake the ethereal solution of the fat or oil with dilute sulphuric acid, filter, ignite the precipitate, and weigh as *lead sulphate*.[1]

P. Schindler[2] found recently considerable amounts of lead in edible oils. Experiments made with non-rancid sesamé oil showed that lead was rapidly attacked. The source of the lead in the commercial edible oils was traced to iron storage vessels which had been coated inside with an alloy of lead and antimony.

Detection and Estimation of Iron

Iron appears to be a normal constituent of the marrow fats of animals, and it would seem that the marrow of young animals contains a higher amount of iron than that of old animals. The amount of iron in the marrow fat decreases with the age of the animal. Fats from other parts of the body, such as muscles, kidneys, cellular tissues, contain small quantities of iron. Traces of iron have also been found in cacao butter, in Japan wax, in beeswax, in spermaceti, and in Chinese wax. Lecithin and cholesterol also tenaciously retain iron. The amount of iron found seems to stand in proportion to the quantity of lecithin present in the substances examined (*W. Glikin*[3]).

As a rule, the determination of iron is unnecessary, except in the case of oils used for dyeing purposes and for currying leather; these oils should be free from iron. Alizarin oil (which usually contains from 15 to 20 per cent of free fatty acids), if kept in iron vessels, is especially liable to be contaminated, and the examination of Turkey-red oils for iron is therefore important.

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[1] Fresenius and Schattenfroh, *Journ. Soc. Chem. Ind.*, 1895, 895 ; *Zeits. f. analyt. Chem.*, 1895 (34), 382.

[2] *Zeits. f. öffentl. Chem.*, 1913, 132.

[3] *Berichte*, 1908, 910.

Emde[1] describes the following convenient method:—The oil is shaken in a graduated cylinder with water acidulated with sulphuric acid. A few drops of potassium ferrocyanide are added, and the whole shaken up with a little ether. The oil dissolves in the ether, and forms a sharply-defined layer on the water. In the presence of iron a more or less dense layer of Prussian blue, containing all the iron, will appear on the border-line between the two liquids. Comparative tests with the same quantities of iron-free oil, water, acid, and potassium ferrocyanide admit of an approximate estimation of the amount of iron.[2]

For accurate estimation it is, of course, necessary to precipitate the iron as hydrated ferric oxide and weigh it as ferric oxide.

Detection of Nickel

The detection of nickel is of special importance in the case of "hydrogenised" ("hardened") fats which are apt to retain traces of the nickel catalyst used in their preparation. The nickel is best detected by incinerating the fat under examination, dissolving the ash in hydrochloric or nitric acid, and testing the solution with diacetyldioxime (dimethylglyoxime) (*Tschugaeff*[3]). An excess of acid should be avoided. The solution is neutralised with ammonia, a little diacetyldioxime in powder is added, and the solution boiled. If a notable amount of nickel is present, a scarlet precipitate is obtained; if only traces of nickel are present, the solution becomes yellowish, and a red precipitate separates on cooling. Thus even one part of nickel in 2,000,000 parts of solution can be detected.[4]

Other inorganic substances which may occur as impurities, or have been added intentionally, are sulphur, phosphorus, and chlorine. They are detected and estimated as follows:—

Qualitative Test for Sulphur

Oils which have been extracted by carbon bisulphide may retain small quantities of sulphur. Some natural oils, such as those belonging to the rape oil group, are apt to retain some sulphur.

Sulphur to the extent of 0·57 per cent has been found in the unsaponifiable matter of cotton seed oil.

Sulphur is detected by saponifying the sample with caustic soda or caustic potash, when sodium or potassium sulphide is formed. On adding to the soap solution an alkaline lead solution, a black or brown precipitate will be obtained.

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[1] *Journ. Soc. Chem. Ind.*, 1888, 591.

[2] For the determination of iron in oleic acid with the aid of adrenalin see Gunn and Harrison, *Pharm. Journ.*, 1907, 25, 181.

[3] *Berichte*, 1905, 2520. Cp. also Fortini, *Chem. Zeit.*, 1912, 1461.

[4] Palladium also is indicated by the "dimethylglyoxime" test (M. Wunder and V. Thüringer, *Zeit. f. analyt. Chem.*, 1913, 101). Although it is not likely that palladium will be used commercially for hydrogenising oils, circumspection must be used in judging from a positive reaction.

A rapid method to detect sulphur is to immerse a bright silver coin into the heated oil. In presence of sulphur the coin will become brown or black.

Sulphuric acid or sulphonated oils (or their fatty acids) cannot be detected by the preceding methods. On washing the sample with water any sulphuric acid present passes into the aqueous layer, and is detected therein with the aid of barium chloride. Sulphonated products obtained by prolonged treatment of oils with sulphuric acid (see Vol. III. Chap. XV. " Turkey-red Oils "), must be first decomposed, either by boiling with hydrochloric acid or by fusing with caustic potash and potassium nitrate.

For the determination of sulphur in sulphur olive oils see Vol. II. Chap. XIV. " Olive Oil."

Quantitative Determination of Sulphur

(*a*) Weigh off carefully a somewhat large quantity of the sample and saponify in a silver dish with alcoholic potash (*Liebig*). Boil down until the mass becomes syrupy, allow to cool, add a few sticks of pure caustic potash and some potassium nitrate—about one-eighth of the weight of the caustic potash—and finally a few drops of water. Heat the mass carefully, with constant stirring—using a silver stirrer—and raise the heat gradually until the mass is fused and has become perfectly white. Then allow to cool, dissolve in water, and transfer to a large beaker, in which the sulphuric acid formed is precipitated in the usual manner with barium chloride. In very accurate work it is preferable to boil out the heated barium sulphate with dilute hydrochloric acid and to weigh again.

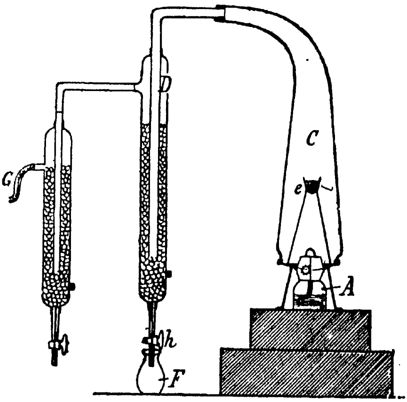

Fig. 7.

(*b*) *Allen*[1] proposes, for the determination of sulphur in oils, an apparatus similar to that used for the estimation of sulphur in coal gas (Fig. 7). Five grams of the oil are mixed with 45 grms. of alcohol and burnt in the lamp A, which is fitted into the wider end of a curved adapter. *e* contains solid ammonium carbonate. The gases pass through C into the condenser D, which is filled with wetted glass balls. The lower end of D is furnished with a glass stop-cock *h* for drawing off the condensed liquid. A second condenser G is attached to D to condense the vapours escaping from D. The upper tubulure of G is connected with an aspirator to produce a slight draught. The flame should be a small one, and should be surrounded by wire gauze to prevent overheating. The liquid drawn from the condensers contains the sulphur as sulphite and sulphate; these are estimated by well-known methods.

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[1] *Analyst*, 1888, 43. Cp. the apparatus adopted by the Metropolitan Gas Referees. In view of the fact that in some petroleums (*Chem. Zeit.*, 1911, 1119) part of the sulphur compounds are not burnt up *pari passu* with the oil, but remain behind, it is necessary to examine the oily residue left in A as well.

Similar contrivances have been described by *Mabery*,[1] by *Heusler*,[2] by *Engler*,[3] by *Kissling*,[4] and by *Schulz*.[5]

Estimation of Phosphorus

In order to estimate the amount of phosphorus in fats containing lecithin, the sample is saponified with alcoholic potash; the alcohol evaporated off, the soap solution diluted with water and shaken out with ether, in order to remove any cholesterol that may be present. The soap solution is then decomposed by a mineral acid, and the fatty acids are separated from the acid liquor. The latter contains the phosphorus as glycero-phosphoric acid (see Chap. III. p. 193). The solution is boiled down to dryness and the residue fused with potassium hydrate and potassium nitrate. The melt is then dissolved in water, the phosphoric acid precipitated by magnesia mixture, and weighed as pyrophosphate. By multiplying the P_2O_5 found by 11·366, the amount is expressed in terms of *lecithin*, $C_{44}H_{90}NPO_9$.

The following table contains the proportions of calculated lecithin in oils and fats :—

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[1] *Journ. Soc. Chem. Ind.*, 1895, 197.

[2] *Ibid.*, 1895, 828.

[3] *Ibid.*, 1896, 383.

[4] *Ibid.*, 1896, 384; cp. also Hempel and Graefe, *Zeits. f. ang. Chem.*, 1904, 1616.

[5] *Ibid.*, 1913, 186.

[TABLE

Oil or Fat.	Phosphorus.	Lecithin calculated from Phosphorus.	Observer.
	Per cent.	Per cent.	
Linseed	...	0·33	Jaeckle
Poppy seed	...	0	,,
Maize	...	1·49	Hopkins
Sorghum	...	0·23	Andrejew
Cotton seed	...	0·0025-0·006	Jaeckle
Sesamé	...	0·005	,,
Wheat	0·25	6·5 (?)	Töpler
Peas[1]	1·17	30·5 (?)	,,
Rape	...	0·11	Jaeckle
Almond	...	0·03	,,
Arachis	...	traces	,,
Egg[2]	...	0·2	Kitt
Cod liver	...	0·005	Jaeckle
Cacao butter	...	0·11	,,
Cocoa nut	...	0·01	,,
Hare	...	0·03	,,
Goose	...	traces	,,
Lard	...	0·022-0·051	,,
,, American	...	0·006	,,
Human	...	0·073-0·084	,,
Beef tallow	...	0·033-0·073	,,
Mutton ,,	...	0·01	,,
Butter	...	0·000-0·014	,,
Bone Marrow, Horse	...	1·450	Glikin[3]
,, ,, Man	...	2-4 (?)	,,
,, ,, Young Pig	...	28-42 (?)	,,

It should, however, be noted that it is not permissible, without further investigation, to calculate the phosphorus thus found to lecithin.[4] Thus, in the case of linseed oil, a considerable amount of the phosphorus is present as calcium or magnesium phosphate.

In order to determine phosphorus in phosphorised oil (see Vol. VIII. Chap. XV.) 5-10 grms. of the sample are dissolved in 100-200 c.c. of acetone; by adding a 10 per cent silver nitrate solution the phosphorus is precipitated as silver phosphide. The precipitate is then filtered off and oxidised with nitric acid. The silver is precipitated with hydrochloric acid, and the phosphoric acid determined in the filtrate by the well-known gravimetric methods.[5]

Katz[6] showed that this method is not exact and that the method proposed by *Straub*[1] (treatment of the phosphorised oil with an excess of a 5 per cent solution of copper sulphate, whereby a black copper phosphide is formed which is oxidised by persistent shaking with air, so that the phosphoric acid may be determined in the solution by means of molybdate, in the usual manner) suffers from several inconveniences. The method proposed by *Katz*[2] is the following: 10 grms. of phosphorised oil are agitated in a separating funnel with 20 c.c. of a 5 per cent aqueous copper nitrate solution until a permanent black emulsion, due to the formation of a copper phosphide (of the formula Cu_2P_2), is produced; 50 c.c. of ether are then added, and 10 c.c. of hydrogen peroxide solution are entered in small portions, until the black emulsion is completely decolourised. The aqueous layer is then run off, and the ethereal layer shaken out three times successively with 10 to 20 c.c. of water; the united aqueous solutions are acidulated with a few drops of hydrochloric acid and evaporated down to 10 or 20 c.c. on the water-bath. If required, the acid liquid is filtered and sufficient ammonia is added to redissolve the precipitate first formed. The phosphoric acid is then precipitated in the usual manner with magnesia mixture.

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[1] Cp. E. Schulze, *Zeits. f. physiol. Chem.*, 1907 (52), 54; *ibid.*, 1908, 981; *Zeits. f. angew. Chem.*, 1908, 1125; cp. also Fahrion, *ibid.*, 1909, 769; Marcusson and Doscher, *Chem. Zeit.*, 1910, 418.

[2] Cp. A. Manasse, *Biochem. Zeits.*, 1906, 246.

[3] *Biochem. Zeits.*, 1907 (4), 235; cp. also Otolski, *ibid.*, 1907, 124.

[4] For the determination of lecithin and lecithin preparations cp. G. Fendler, *Apoth. Zeit.*, 1905, No. 3; E. Schulze, *Chem. Zeit.*, 1908, 981; M. Morigi, *Bull. Chim. Farm.*, 1909 (48), 753; W. Fresenius and L. Grünhut, *Zeits. f. analyt. Chem.*, 1910, 90; P. Salzmann, *Apoth. Zeit.*, 1911 (26), 949; K. Virchow, *Chem. Zeit.*, 1912, 906; J. D Riedel, *Chem. Zentralbl.*, 1912, i. 1794; J. C. Schippers, *Biochem. Zeits.*, 1912 (40), 189; P. Freundler, *Bull. Soc. Chim. de France*, 1912 (11), 1041; R. Cohn, *Zeit. f. öffentl. Chem.*, 1913, 54.

[5] Cp. Louise, *Compt. rend.*, 1899 (129), 394; *Journ. Pharm. Chim.* 10, 241. Fränkel, *Pharm. Post.*, 1901 (34), 117.

[6] *Arch. d. Pharm.*, 1904, 121.

In case the hydrogen peroxide employed contains phosphoric acid (usually added to render it more stable), the amount of such phosphoric acid must be ascertained in a blank test.

If the amount of oxidised phosphorus in a phosphorised oil be required, the oil must be first extracted with water which has been saturated with carbon dioxide. The phosphorus is then determined both in the aqueous extract and in the phosphorised oil.

Katz prepared a number of phosphorised oils by placing dried phosphorus with oil in a bottle containing an atmosphere of carbon dioxide, warming the contents slowly in a water-bath until the phosphorus had melted, and shaking the mixtures (in a shaking machine) for one to two hours. The amounts of dissolved phosphorus were determined by the above-described method with the following result:[3]—

Phosphorised Oil from	Phosphorus. Per cent.
Linseed oil	1·15
Poppy seed oil	1·10
Sesamé oil	1·06
Rape oil	1·16
Almond oil	1·13
Arachis oil	1·20
Olive oil	1·085
Castor oil	0·70
Cod liver oil	1·13

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[1] *Arch. d. Pharm.*, 1903; cp. also *Zeits. f. anorg. Chem.*, 1903, 460.

[2] *Ibid.*, 1904, 121.

[3] For a criticism of Katz's method cp. H. Enell, *Pharm. Zeit.*, 1905 (50), 601. The process proposed by Enell has in its turn been criticised by E. Rupp, *ibid.*, 1905, 621; cp. further, P. Bohrisch, *Pharm. Zentralbl.*, 1909 (50), 19; O. Frey, *Pharm. Post*, 1910 (December).

Estimation of Chlorine, Bromine, Iodine

Fats bleached by means of chlorine are apt to retain small quantities of the bleaching agent.

Benedikt and Zikes[1] determine small quantities of chlorine by allowing 25 grms. of the oil or liquefied fat to drop slowly from a separating funnel into a combustion tube filled with lime. The estimation is then completed in the well-known manner employed in determining chlorine in organic substances.

In the same manner bromine and iodine,[2] which occur legitimately in brominated and iodised fats, may be determined (cp. Vol. III. Chap. XV.). For the determination of bromine in ether-insoluble bromides see Chap. VIII. *Tolman*[3] uses *Pringsheim's* method (see below) of oxidising with sodium peroxide in an iron crucible or in the bomb of a calorimeter. Any bromate formed is reduced by a concentrated solution of sodium sulphite. The bromide is then precipitated, after acidification with sulphuric acid, with silver nitrate. In order to prevent precipitation of silver sulphate the solution is made strongly acid with nitric acid.

For a rapid method of detecting the presence of halogens, phosphorus, arsenic, and sulphur in organic compounds by means of sodium peroxide, see Pringsheim, *Berichte*, 1904, 2155; cp. also *Journ. Amer. Chem. Soc.*, 1904 (31), 386.

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[1] *Journ. Soc. Chem. Ind.*, 1894, 984.

[2] Cp. *Chem. Revue*, 1904, 280.

[3] *Journ. Ind. and Eng. Chem.*, 1909, 341.

CHAPTER V

PHYSICAL METHODS OF EXAMINING OILS, FATS, AND WAXES

THE examination of the physical properties of oils, fats, and waxes affords, in many cases, valuable information, and lends important aid in the identification of samples, as also in the detection of adulteration.

The *specific gravities* of the oils, fats, and waxes, and their melting and solidifying points, especially those of their fatty acids, furnish, as a rule, the most valuable criteria.

Thanks to the construction of handy apparatus, the determination of the *refractive index* has become one of the most frequently practised preliminary methods of examination for purity, and whenever the necessary apparatus is available it should be employed, as this method combines in many cases rapidity of observation with certainty of result.

Examination for the presence of *optically active* substances has hitherto been somewhat neglected; by this means it is, however, possible to identify rapidly several fats (of a poisonous character) as also to detect some adulterants with certainty.

Microscopic examination has recently come more to the fore, and promises to offer great assistance in the detection of mixed glycerides. Other optical methods, such as *spectroscopic* and *colorimetric* examination, may furnish valuable information in some cases.

The behaviour of oils and fats with *solvents* often serves as a valuable confirmation of indications furnished by other tests. Considering the great similarity in the chemical composition of the individual oils and fats, it is indispensable to employ systematically a series of solvents (cp. Chap. XII.).

In some cases, especially in the examination of lubricating oils, the determination of the *viscosity* and the determination of the flash point will prove of assistance.

A number of other physical properties and their determination will be referred to for the sake of completeness, although these determinations can hardly be carried out in an ordinary analytical laboratory.

The physical properties, and the methods of determining them, will be described under the following heads in the order of their importance from an analytical point of view, *i.e.* in the order of their utility for the identification of individual oils and fats and the recognition of their purity :—

1. Specific Gravity.
2. Melting and Solidifying Points.
3. Refractive Index.
4. Rotatory Power.
5. Microscopic Appearance (Micrography).
6. Spectroscopic Examination.
7. Colorimetry.
8. Viscosity.
9. Solubility.
10. Electrical Conductivity.
11. Calorimetric Examination—Specific Heat.

Other physical methods, such as the determination of diffusion coefficients,[1] capillary analysis,[2] cryoscopic determination,[3] dilatability,[4] are not described in detail here, as they do not furnish at present more decisive results than can be obtained by less complicated methods. Some other physical methods, such as the determination of cohesion figures,[5] emulsifying powers, miscibility curves,[6] etc., being entirely useless for practical purposes, are omitted.

1. Specific Gravity

The specific gravity of the liquid fats and waxes may be ascertained at the ordinary temperature by the well-known methods adopted for any other liquid, viz. by means of a hydrometer, picnometer, or the hydrostatic balance.

It should hardly be necessary to emphasise here the importance of ascertaining the accuracy and delicacy of the hydrometer to be used. The readiest indications will be obtained by means of hydrometers referring to the density of water, whilst the use of *Twaddell's* hydrometer involves a calculation, simple though it be.

On the Continent and in America various hydrometers, based on an arbitrary scale, are used in commerce and are still employed by custom-house officials. These hydrometers, gauged for a definite temperature, express the densities in " degrees " ; the true specific gravities *s* can be calculated by means of the subjoined table, *n* denoting the number of " degrees." It should, however, be pointed out that there are a number of different Baumé hydrometers in commerce (no less than 36 different scales), so that due allowance must be made for deviations from the actual standard used by Baumé. Baumé's starting-points were pure water and a 10 per cent salt solution which, according to *Gerlach*, has the specific gravity 1·07335 at 15° C. and 1·07311 at 17·5° C. (*Chandler* gives 1·0737665 for the temperature 12·5° C.)

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[1] Zaloziecki, *Chem. Rev.*, 1897, 220, 229.

[2] Braconnot in 1815. Goppelsroeder, *Capillaranalyse*, Bâle, 1901, and *Anregung zum Studium der Capillaranalyse*, Bâle, 1906. Cp. also *Chem. Zeit.*, 1909, 1333.

[3] Robertson, *Journ. Chem. Soc.*, 1903, 1425. Pailheret, *Bull. Soc. Chim. de France*, 1909, 425 (cp. Butter Fat, Vol. II. Chap. XIV.).

[4] Thörner, *Zeits. f. Chem. Apparatenkunde*, 1908, 165.

[5] Cp. myelin-forms. A. Müller, *Allgemeine Chemie der Kolloide*, 1907, p. 88.

[6] Cp. E. Louis, *Compt. rend.*, 1909 (149), 284.

In the United States of America frequently the formula $s = \frac{145}{135 - n}$ (at 60° F.) is used in place of the formula given in the following table :— $s = \frac{146{\cdot}3}{146{\cdot}3 - n}$ for liquids heavier than water.

The American formula $s = \frac{140}{130 + n}$ employed for liquids lighter than water leads to 1·0769 as the specific gravity of a 10 per cent salt solution.

The tables given on the following pages should, therefore, be used with discretion. The table for "liquids lighter than water" given on page 303 is based on the American formula.

It must, therefore, be understood that the true specific gravities calculated from the formulæ given in the table do not always coincide with those determined in a direct manner.

Hydrometer.	Temperature.	For Liquids heavier than Water.	For Liquids lighter than Water.
Balling . .	17·5° C.	$s = \frac{200}{200 - n}$	$s = \frac{200}{200 + n}$
Baumé I . .	12·5° C.	$s = \frac{144}{144 - n}$	$s = \frac{144}{134 + n}$
Baumé II . .	15° C.	$s = \frac{144{\cdot}3}{144{\cdot}3 - n}$	$s = \frac{144{\cdot}3}{134{\cdot}3 + n}$
Baumé III . .	17·5° C.	$s = \frac{146{\cdot}78}{146{\cdot}78 - n}$	$s = \frac{146{\cdot}78}{136{\cdot}78 + n}$
Beck . . .	12·5° C.	$s = \frac{170}{170 - n}$	$s = \frac{170}{170 + n}$
Brix . . .	12·5° R. 15·625° C.	$s = \frac{400}{400 - n}$	$s = \frac{400}{400 + n}$
Cartier . .	12·5° C.	$s = \frac{136{\cdot}8}{126{\cdot}1 - n}$	$s = \frac{136{\cdot}8}{126{\cdot}1 + n}$
Fischer . .	12·5° R. 15·625° C.	$s = \frac{400}{400 - n}$	$s = \frac{400}{400 + n}$
Gay-Lussac . .	4° C.	$s = \frac{100}{n}$	$s = \frac{100}{n}$
E. G. Greiner .	12·5° R. 15·625° C.	$s = \frac{400}{400 - n}$	$s = \frac{400}{400 + n}$
Stoppani . .	12·5° R. 15·625° C.	$s = \frac{166}{166 - n}$	$s = \frac{166}{166 + n}$
Twaddell . .	...	$s = \frac{\frac{n}{2} + 100}{100}$	

Hydrometers should only be employed where rapidity is of greater importance than accuracy. In such cases the following tables will be found useful :—

Comparison of the Hydrometer Degrees, according to Baumé and Twaddell, with Specific Gravities

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
0	0	1·000	6·7	10	1·050	13·6	21	1·105
0·7	1	1·005	7·0	10·2	1·052	14·0	21·6	1·108
1·0	1·4	1·007	7·4	11	1·055	14·2	22	1·110
1·4	2	1·010	8·0	12	1·060	14·9	23	1·115
2·0	2·8	1·014	8·7	13	1·065	15·0	23·2	1·116
2·1	3	1·015	9·0	13·4	1·067	15·4	24	1·120
2·7	4	1·020	9·4	14	1·070	16·0	25	1·125
3·0	4·4	1·022	10·0	15	1·075	16·5	26	1·130
3·4	5	1·025	10·6	16	1·080	17·0	26·8	1·134
4·0	5·8	1·029	11·0	16·6	1·083	17·1	27	1·135
4·1	6	1·030	11·2	17	1·085	17·7	28	1·140
4·7	7	1·035	11·9	18	1·090	18·0	28·4	1·142
5·0	7·4	1·037	12·0	18·2	1·091	18·3	29	1·145
5·4	8	1·040	12·4	19	1·095	18·8	30	1·150
6·0	9	1·045	13·0	20	1·100	19·0	30·4	1·152

[TABLE

Comparison of the Hydrometer Degrees, according to Baumé and Twaddell, with Specific Gravities—continued

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
19·3	31	1·155	37·8	71	1·355	51·5	111	1·555
19·8	32	1·160	38·0	71·4	1·357	51·8	112	1·560
20·0	32·4	1·162	38·2	72	1·360	52·0	112·6	1·563
20·3	33	1·165	38·6	73	1·365	52·1	113	1·565
20·9	34	1·170	39·0	74	1·370	52·4	114	1·570
21·0	34·2	1·171	39·4	75	1·375	52·7	115	1·575
21·4	35	1·175	39·8	76	1·380	53·0	116	1·580
22·0	36	1·180	40·0	76·6	1·383	53·3	117	1·585
22·5	37	1·185	40·1	77	1·385	53·6	118	1·590
23·0	38	1·190	40·5	78	1·390	53·9	119	1·595
23·5	39	1·195	40·8	79	1·395	54·0	119·4	1·597
24·0	40	1·200	41·0	79·4	1·397	54·1	120	1·600
24·5	41	1·205	41·2	80	1·400	54·4	121	1·605
25·0	42	1·210	41·6	81	1·405	54·7	122	1·610
25·5	43	1·215	42·0	82	1·410	55·0	123	1·615
26·0	44	1·220	42·3	83	1·415	55·2	124	1·620
26·4	45	1·225	42·7	84	1·420	55·5	125	1·625
26·9	46	1·230	43·0	84·8	1·424	55·8	126	1·630
27·0	46·2	1·231	43·1	85	1·425	56·0	127	1·635
27·4	47	1·235	43·4	86	1·430	56·3	128	1·640
27·9	48	1·240	43·8	87	1·435	56·6	129	1·645
28·0	48·2	1·241	44·0	87·6	1·438	56·9	130	1·650
28·4	49	1·245	44·1	88	1·440	57·0	130·4	1·652
28·8	50	1·250	44·4	89	1·445	57·1	131	1·655
29·0	50·4	1·252	44·8	90	1·450	57·4	132	1·660
29·3	51	1·255	45·0	90·6	1·453	57·7	133	1·665
29·7	52	1·260	45·1	91	1·455	57·9	134	1·670
30·0	52·6	1·263	45·4	92	1·460	58·0	134·2	1·671
30·2	53	1·265	45·8	93	1·465	58·2	135	1·675
30·6	54	1·270	46·0	93·6	1·468	58·4	136	1·680
31·0	54·8	1·274	46·1	94	1·470	58·7	137	1·685
31·1	55	1·275	46·4	95	1·475	58·9	138	1·690
31·5	56	1·280	46·8	96	1·480	59·0	138·2	1·691
32·0	57	1·285	47·0	96·6	1·483	59·2	139	1·695
32·4	58	1·290	47·1	97	1·485	59·5	140	1·700
32·8	59	1·295	47·4	98	1·490	59·7	141	1·705
33·0	59·4	1·297	47·8	99	1·495	60·0	142	1·710
33·3	60	1·300	48·0	99·6	1·498	60·2	143	1·715
33·7	61	1·305	48·1	100	1·500	60·4	144	1·720
34·0	61·6	1·308	48·4	101	1·505	60·6	145	1·725
34·2	62	1·310	48·7	102	1·510	60·9	146	1·730
34·6	63	1·315	49·0	103	1·515	61·0	146·4	1·732
35·0	64	1·320	49·4	104	1·520	61·1	147	1·735
35·4	65	1·325	49·7	105	1·525	61·4	148	1·740
35·8	66	1·330	50·0	106	1·530	61·6	149	1·745
36·0	66·4	1·332	50·3	107	1·535	61·8	150	1·750
36·2	67	1·335	50·6	108	1·540	62·0	150·6	1·753
36·6	68	1·340	50·9	109	1·545	62·1	151	1·755
37·0	69	1·345	51·0	109·2	1·546	62·3	152	1·760
37·4	70	1·350	51·2	110	1·550	62·5	153	1·765

Comparison of the Hydrometer Degrees, according to Baumé and Twaddell, with Specific Gravities—continued

Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.	Baumé.	Twaddell.	Specific Gravity.
62·8	154	1·770	65·0	164	1·820	67·0	173	1·865
63·0	155	1·775	65·2	165	1·825			
63·2	156	1·780	65·5	166	1·830			
63·5	157	1·785	65·7	167	1·835			
63·7	158	1·790	65·9	168	1·840			
64·0	159	1·795	66·0	168·4	1·842			
64·2	160	1·800	66·1	169	1·845			
64·4	161	1·805	66·3	170	1·850			
64·6	162	1·810	66·5	171	1·855			
64·8	163	1·815	66·7	172	1·860			

Degrees Baumé,[1] *for Liquids lighter than Water at* 15·5° *C.* = 60° *F.*

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
10	1·0000	24	0·9090	38	0·8293	51	0·7734	64	0·7216
11	0·9929	25	0·9032	39	0·8284	52	0·7692	65	0·7179
12	0·9859	26	0·8974	40	0·8235	53	0·7650	66	0·7142
13	0·9790	27	0·8917	41	0·8187	54	0·7608	67	0·7106
14	0·9722	28	0·8860	42	0·8139	55	0·7567	68	0·7070
15	0·9655	29	0·8805	43	0·8092	56	0·7526	69	0·7035
16	0·9589	30	0·8750	44	0·8045	57	0·7486	70	0·7000
17	0·9523	31	0·8695	45	0·8000	58	0·7446	75	0·6829
18	0·9459	32	0·8641	46	0·7954	59	0·7407	80	0·6666
19	0·9395	33	0·8588	47	0·7909	60	0·7368	85	0·6511
20	0·9333	34	0·8536	48	0·7865	61	0·7326	90	0·6363
21	0·9271	35	0·8484	49	0·7821	62	0·7290	95	0·6222
22	0·9210	36	0·8433	50	0·7777	63	0·7253	100	0·6087
23	0·9150	37	0·8383						

The specific gravity is usually determined by means of a picnometer of one kind or another. Of these the ordinary specific gravity bottle, consisting of a plain flask with a stopper having a capillary perforation, will be found useful for commercial work; with care, even the fourth decimal can be determined accurately.

A high degree of accuracy is obtained with *Sprengel's* picnometer (Fig. 8). This is a U-tube made of thin glass, ending in two capillary tubes *a* and *b* bent at right angles and ground at their ends, so as to fit into two glass caps (the latter are not shown in the figure). The inner diameter of tube *b*, bearing the mark *m*, is about 0·5 mm., whilst that of tube *a* is less, and should not exceed 0·25 mm. This point should be noted, as this essential feature of the *Sprengel* tube is lost sight of by some makers. The tube is filled by connecting *a* with a glass bulb, and aspirating the air with the aid of india-rubber tubing, whilst *b* is immersed in the oil under examination. If the glass bulb be chosen sufficiently large, the *Sprengel* tube will be filled automatically on closing the india-rubber tubing with the fingers. As soon as the oil enters the bulb, the *Sprengel* tube is detached from it, and the picnometer allowed to assume the desired temperature (see below). The liquid expands or contracts *in the tube b only*, *i.e.* in the direction of the least resistance, whilst the capillary tube *a* always remains full. If the meniscus of the liquid is found to be beyond the mark *m*, a little oil can be abstracted by means of a roll of filter-paper applied to the end of *a*; if, however, the tube contains too little, *a* may be touched with a glass rod which has been dipped into the oil, when some oil is drawn in, the liquid moving forward in the tube *b*. In this manner the volume can be adjusted easily. Finally, the two glass caps are put on the tubes *a* and *b*; the picnometer is then ready for weighing.

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[1] Cp. p. 300.

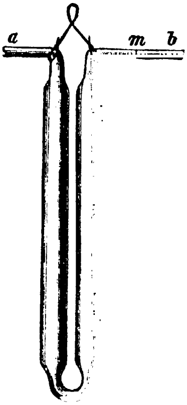

Fig. 8.

If the weights found be reduced to weights *in vacuo*, the specific gravity will be correct to the fourth decimal, the error only affecting the fifth decimal. So high a degree of accuracy is but rarely required; in the commercial examination of glycerin, however (cp. Vol. III. Chap. XV.), the *Sprengel* tube is frequently employed.

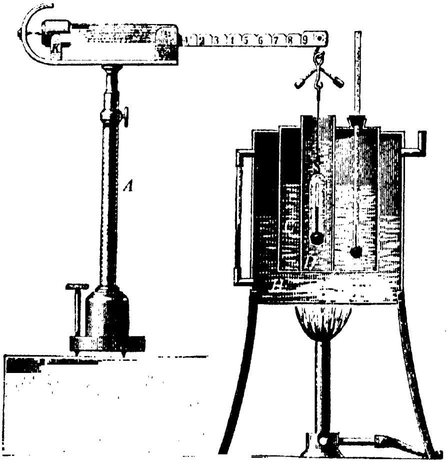

Fig. 9.

Mohr's (hydrostatic) balance is not so accurate, but still quite satisfactory for ordinary purposes, and is largely used on account of its convenience. One form of this instrument is shown in Fig. 9, which requires no further explanation.[1] The plummet, it may be added, displaces exactly 10 c.c., and therefore the weights put on the lever to restore equilibrium give exactly the weight of 10 c.c. of the substance. Thus all calculation is avoided, the specific gravity being read direct from the weights used.

For the determination of the specific gravity of viscous oils[2] (such as boiled oils) at the ordinary temperature, the picnometer described by *Brühl* (Fig. 10) is useful. A pipette containing the viscous substance is inserted air-tight in the flask by means of an india-rubber tube, and the flask is exhausted by connecting the side tube with a filter pump.[3]

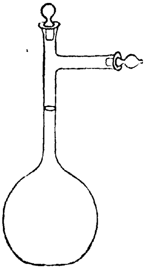

Fig. 10.

In specific gravity determinations, care must be taken that the temperature throughout the entire mass of the oil be the same. It will be found best, after having brought the oil to the standard temperature, to keep it for some time—ten minutes at least —in a sufficiently large water-bath having the same temperature. The temperature should be observed by means of an accurate thermometer. The standard temperature in this country is 60° F. = 15·5° C.

The weight of the oil should be compared with that of an equal volume of water taken at the same temperature. It is customary to consider the weight of that volume of water at 15·5° C. as unity. In exact work the weight should be reduced to that *in vacuo* and referred to water at 4° C. (cp. Vol. III. Chap. XV. " Glycerin Manufacture ").

If the quantity of the sample is too small to fill a picnometer, the specific gravity may be deduced from that of a dilute alcohol, in which a drop of the oil will just float (cp. p. 308).

E. Bellmer[4] suggests the following *modus operandi* :—Place a drop of oil in 2 c.c. of 98-99 per cent alcohol, and add carefully, drop by drop, distilled water from a burette until the drop of oil just commences to float in the dilute alcohol.

In the following table, due to *Bellmer*, the specific gravity can be found from the amount of water added, provided that the " titration " is being carried out at 15° C.

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[1] Cp. Thörner, *Journ. Soc. Chem. Ind.*, 1895, 44 (Illustration).

[2] With regard to the determination of the specific gravity of viscous petroleum oils cp. J. M'Connell Sanders, *Proceed. Chem. Soc.*, 1911, 250.

[3] For a modification of this apparatus cp. L. v. Kreybig, *Chem. Zeit.*, 1911, 1120.

[4] *Chem. Zeit.*, 1911, 997.

[TABLE

Water. c.c.	Specific Gravity.	Water. c.c.	Specific Gravity.	Water. c.c.	Specific Gravity.	Water. c.c.	Specific Gravity.
0·1	0·8178	1·1	0·9050	2·1	0·9376	3·1	0·9537
0·2	0·8331	1·2	0·9091	2·2	0·9397	3·2	0·9548
0·3	0·8456	1·3	0·9133	2·3	0·9417	3·3	0·9558
0·4	0·8563	1·4	0·9173	2·4	0·9436	3·4	0·9568
0·5	0·8678	1·5	0·9209	2·5	0·9453	3·5	0·9577
0·6	0·8739	1·6	0·9243	2·6	0·9469	3·6	0·9587
0·7	0·8812	1·7	0·9273	2·7	0·9485	3·7	0·9595
0·8	0·8880	1·8	0·9301	2·8	0·9499	3·8	0·9603
0·9	0·8940	1·9	0·9329	2·9	0·9512	3·9	0·9610
1·0	0·8995	2·0	0·9353	3·0	0·9525	4·0	0·9617

Obviously, the determination of the specific gravity of fats and waxes which are semi-solid at the standard temperature, leads to complications and difficulties (see below), which are avoided by adopting as the standard a temperature at which the substances are fluid. *Bell*, as also *Muter*, somewhat arbitrarily proposed the temperature of 100° F. =37·75° C., whilst others prefer the temperature of boiling water.

For correct determinations at elevated temperatures it is best to use a *Sprengel* tube. The tube is immersed in boiling water in such a manner that only the ends of the capillary tubes protrude. After about twenty minutes' boiling the glass caps are placed on the tubes, the *Sprengel* tube is removed from the water-bath, wiped dry, and weighed after cooling. The weight of the fat may be referred to the weight of water at the boiling point, or, as is done by most observers, to the weight of water at 15·5° C. The unity chosen must, of course, be distinctly stated. For scientific purposes water at 4° C. should be taken as unity.

The employment of the hydrostatic balance at higher temperatures necessitates the use of a somewhat complicated arrangement. The balance recommended by *Bell* is shown (partly in section) in Fig. 9. It is designed for the temperature of 100° F. D is a glass tube containing the sample of fat; C is filled with paraffin wax, and is surrounded by the water-jacket B.

In cases where, for some special reason, neither the temperature of 15·5° C. nor 100° C. can be employed, a correction must be made, which depends on the coefficient of expansion of the particular oil under examination. *Allen* [1] determined the rate of expansion of a number of oils and fats, by taking their densities at 98° C. and 15·5° C., and dividing the difference of these densities by the difference of the temperatures. Thus he obtained the correction to be made for a variation of 1° C. Although this method is not scientifically correct, inasmuch as it rests on the assumption that the rate of expansion does not vary between 15·5° C. and 98° C. [the mean coefficient of expansion differs from the true one as the quotient of differences from the differential quotient], the values obtained by *Allen* will satisfy practical requirements. The correction for 1° C. was found to vary for seventeen kinds of fat between the limits 0·000615 and 0·000665. Only whale oil (two samples of which had been examined many years ago when commercial whale oil was a much more impure article than it is at present) showed apparently an abnormal rate of expansion, the corrections given by *A. H. Allen and C. M. Wetherill* being respectively 0·000697 and 0·000722. These values, therefore, require verification with such specimens as are at present readily obtainable in commerce. *Allen* proposed to take as the mean correction for one degree Celsius 0·00064 (or for one degree Fahrenheit 0·00035). If the density of an oil be 0·9207 at 22° C., its density at 15·5° C. is as follows:—The difference of the temperatures is $22-15{\cdot}5=6{\cdot}5$; hence the correction $6{\cdot}5 \times 0{\cdot}00064=0{\cdot}00416$. This added to 0·9207 gives 0·92486 as the specific gravity at 15·5° C.[1]

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[1] *Commercial Organic Analysis*, ii. 19.

The coefficient of expansion of an oil may also be found by the "picnometric method" by dividing the correction for one degree of temperature by the specific gravity of the oil at the lower temperature. It should, however, be borne in mind that the volume of the picnometer varies with the temperature, and that it is therefore necessary to make a correction for the expansion of the glass.

For the determination of the specific gravity of **solid** fats and waxes, it is convenient to use a temperature at which they are liquid,

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[1] C. H. Wright (*Journ. Soc. Chem. Ind.*, 1907, 26, 513-515) calculated the numerical value of the approximate modulus of expansion, m, for the temperature correction applicable to the specific gravities of all oils, fats, and waxes, from the data determined by Allen. If S_o, S_t, and S_T represent the specific gravities (water at 15·5° C. = 1) of the same oil or fat at 0°, $t°$, and T° C. respectively, then we have: $S_t=S_o(1-mt)$, and $S_T=S_o(1-mT)$. On dividing the first equation by the second we obtain $\frac{S_t}{S_T}=\frac{1-mt}{1-m_T}$. The mean value for m in the case of the thirty oils, fats, and waxes examined by Allen is 0·000718. Hence $S_t/S_T=1-0{\cdot}000718t/1-0{\cdot}000718T$; and for $t=15{\cdot}5°$ C.

$$S15{\cdot}5=S_T\frac{0{\cdot}988871}{1-0000718}T.$$

The following table shows the value of this factor for each degree from 10° to 25° C., hence the specific gravity determined at a temperature other than 15·5° C. may be rapidly corrected to 15·5° C.:—

At °C.	Factor.	At °C.	Factor.
10	$\frac{1}{1{\cdot}00389}$	18	1·00177
11	$\frac{1}{1{\cdot}00318}$	19	1·00248
12	$\frac{1}{1{\cdot}00248}$	20	1·00319
13	$\frac{1}{1{\cdot}00177}$	21	1·00391
14	$\frac{1}{1{\cdot}00106}$	22	1·00462
15	$\frac{1}{1{\cdot}00035}$	23	1·00534
16	1·00035	24	1·00605
17	1·00106	25	1·00677

e.g. 100° C. *Gintl's*[1] picnometer, shown in Fig. 11, may be used for determinations at the ordinary temperature. It consists of a small cylindrical, flat-bottomed vessel, *I*, made of very thin glass and provided with a ground-glass cover. The vessel fits into the frame *a* (Fig. 12), the screw *b* serving to press the glass cover tightly on the cylinder. The vessel is weighed first empty and then filled with water at the standard temperature. After emptying the water and drying carefully, *I* is completely filled with the melted fat, and allowed to cool to the standard temperature. The glass cover is then carefully placed on *I*, so as to squeeze out the surplus fat, and is secured in its position by means of the screw. The fat on the outside is carefully removed with the aid of ether and the vessel weighed again.

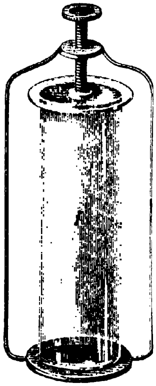

Fig. 11.

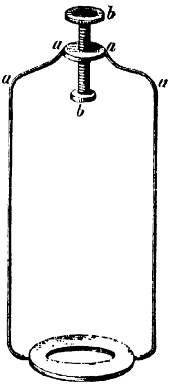

Fig. 12.

Another method, proposed originally by *Fresenius and Schulze*, will be found useful in the case of waxes. It is best employed in the form given it by *Chattaway and Allen.*[2] The wax is melted on a watch-glass placed on boiling water, and small pieces are cut from the *spontaneously* cooled mass.[3] They are brushed over with a wet brush in order to remove adherent air-bubbles, and carefully placed in dilute alcohol by means of a pair of forceps. It is convenient to keep a set of standard mixtures of alcohol and water having specific gravities of 0·960, 0·961, 0·962, and so on up to 0·970 at 15·5° C. That liquid in which the wax globules will just float has the same specific gravity as the sample.

A somewhat complicated apparatus for the determination of the densities of soft fats was proposed by *Zawalkiewicz.*[4]

Instead of determining the specific gravity by weighing a definite volume according to the equation $d = \frac{m}{v}$ (where d denotes the density, m the weight, and v the volume), *Zaloziecki*[5] proposed to measure the volume of the fatty acids derived from a known weight of fat. Evidently this is no new constant, as from the formula just given, it follows that $v = \frac{m}{d}$, and no further information is gained than that afforded by the determination of the specific gravity of the fat. The volume of the fatty acids is referred to the weight of fat, and it becomes therefore simply a question whether the method proposed by *Zaloziecki* is more expeditious than the weighing of the original fat in a picnometer. There can be no doubt that *Zaloziecki's* method is more cumbersome. For this reason, and for the more cogent one that a serious error is introduced by the solubility of the volatile fatty acids, this method cannot be recommended.

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[1] *Dingl. Polyt. Journ.*, 1869 (194), 42.

[2] *Commercial Organic Analysis*, 1880, ii. 184. Cp. also A. Lissner, *Chem. Zeit.*, 1910, 657.

[3] The German Pharmacopœia directs to form spheres of the waxes. Cp. E. Richter, *Apotheker Zeit.*, 1911 (26), 187; G. Fromme, *ibid.*, p. 402.

[4] *Journ. Soc. Chem. Ind.*, 1894, 839.

[5] *Chem. Revue*, 1897, 119.

Although the specific gravity of the individual oils, fats, and waxes furnishes an important and characteristic number, which frequently serves as an additional means of identification, or as a verification of results arrived at by other methods, the specific gravity numbers in themselves afford very little discriminating data for purposes of classification, and the importance that was ascribed to the specific gravity numbers in earlier works was much overrated. This may be exemplified by the extensive use of "oleometers" purporting not only to discriminate between different oils, but even to aid in the detection of adulteration. To show that the specific gravity number alone is of limited value as a sorting test, I append the following table, in which the specific gravities of some of the most important oils, fats, and waxes are placed opposite the classes adopted in this treatise :—

Specific Gravities of the most important Oils,

	0·876-0·883	0·900-0·910	0·913-0·916	0·916-0·920
FATTY OILS :—				
Vegetable oils—				
Drying oils . . .	..	..	..	..
Semi-drying oils . .	..	..	Rape oil group	..
Non-drying oils . . .	..	..	..	Almond oil, Arachis oil, Olive oil
Animal oils—				
Marine animal oils—				
Fish oils . . .	..	..	..	..
Liver oils . . .	..	..	..	..
Blubber oils . .	..	..	..	..
Terrestrial animal oils	..	..	Egg oil, Neat's Sheep's Horses'	.. foot oil foot oil foot oil
SOLID FATS :—				
Vegetable fats . . .	..	..	..	..
Animal fats—				
Semi-drying fats . .	..	..	..	Horse fat
Non-drying fats . .	..	..	Bone fat	..
LIQUID WAXES . . .	Sperm oil, Arctic sperm oil			
SOLID WAXES :—				
Vegetable waxes . .	..	..	..	..
Animal waxes . . .	..	..	..	..

Fats, and Waxes, at 15·5° *C.*

0·920-0·925	0·925-0·935	0·935-0·940	0·940-0·950	0·950-0·960	0·960-0·970	0·970-0·999
Hemp seed oil, Soya bean oil, Maize oil, Cotton seed oil, Sesamé oil, etc.	Linseed oil	Tung	oil			
..	..	..	..	Castor oil, Croton oil		
Herring oil	Japan fish oil, Menhaden oil					
Cod li	ver oil,					
Skate li	ver oil,					
e	tc.					
Whale oil	Porpoise oil					
Palm oil	Laurel oil Cocoa nut oil, Palm kernel oil	..	Nutmeg	butter	..	Japan wax Myrtle wax
				Cacao	butter	
..	..	Lard				
		Tal	low			
		Butter fat				
..	..	..	..	..	..	Carnaüba wax
..	..	..	..	..	Beeswax, Insect wax	

Although the liquid waxes on the one hand, and the solid waxes (including the wax-like fats) on the other hand, may readily be recognised by their specific gravities, much overlapping will be noticed. Some oils and fats fall within more than one subdivision, and the most heterogeneous fats, as regards chemical composition and other properties, range themselves in one and the same vertical column. A complete list of specific gravities will be found in Vol. II. Chap. XIV., under the heading of each individual oil, fat, and wax. A complete enumeration of the specific gravities, furnishing a rapid survey of individual oils, fats, and waxes, is contained in Table 24 of my "*Laboratory Companion.*"

The iodine value being the basis of the classification adopted throughout this treatise, it may be interesting to inquire whether any definite connection can be traced between the iodine value and the specific gravity. As a high iodine value indicates a high proportion of unsaturated glycerides, and the greater the unsaturation of the fatty acids, the higher their specific gravity, some parallelism may be expected. Speaking broadly, such may indeed be traced through the three main classes of oils, viz. the drying, semi-drying, and non-drying oils. Due regard must, however, be paid to the chemical constitution of the fatty acids; thus castor oil deviates entirely from the rough approximation to the general rule to which the several classes just mentioned seem to conform. Nor can a definite rule be expected to hold good, as differences of climatic conditions, race, etc., produce a difference in the specific gravity, as well as in the iodine value. *Wijs* endeavoured to trace a correspondence between the specific gravity and the iodine value in the case of linseed oil, sesamé oil, and arachis oil. Whereas in these cases high specific gravities appear to correspond to high iodine values, the rule seems to break down in the case of cotton seed oil. More information on this subject will be found under each individual oil in Vol. II. Chap. XIV.

The influence which glycerides of soluble fatty acids have on the specific gravities of some solid fats is shown more particularly by the following two tables. It will be seen that glycerides of soluble acids increase the specific gravity.

A. *Fats, free from Glycerides of Soluble Volatile Fatty Acids*

Class of Fat.	Kind of Fat.	Specific Gravities at 100° C. (Water at 15° C. = 1.)
Vegetable Fats	Cacao butter	0·857
	Palm oil	0·857
	Japan wax	0·8755
Animal Fats	Lard	0·861
	Tallow (beef and mutton)	0·860
	Horse fat	0·861
	Oleomargarine	0·859

B. *Fats, containing Glycerides of Soluble Volatile Fatty Acids*

Class of Fat.	Kind of Fat.	Specific Gravities at 100° C. (Water at 15° C. = 1.)
Vegetable fats	Cocoa nut oil Palm nut oil	0·8736 0·8731
Animal fats	Butter fat	0·865-0·868

The presence of free fatty acids in oils and fats naturally influences the specific gravity number to some extent. Inasmuch as the free fatty acids, on exposure to the atmosphere, undergo changes more rapidly than their glycerides, it frequently occurs that the specific gravities of oils and fats containing free fatty acids rise with the increase in the amount of free fatty acids. A definite relation, however, does not exist between the proportion of free fatty acids and the specific gravity, and the reverse occurs with equal frequency.[1] This is shown by the numbers contained in the following table:—

No.	Kind of Oil.	Free Fatty Acids Per cent.	Specific Gravity at 15·5° C. (Water at 15·5° C. = 1.)	Observer.
1	Olive oil, No. 2, freed from fatty acids	0·0	0·9152	Thomson and Ballantyne[2]
2	Olive oil	3·86	0·9148	,, ,,
3	Olive oil (edible)	4·15	0·9151	,, ,,
4	Olive oil	5·19	0·9168	,, ,,
5	Olive oil (Gioja).	9·42	0·9156	,, ,,
6	Olive oil (for dyeing). . . .	9·67	0·9154	,, ,,
7	Olive oil	11·28	0·9145	,, ,,
8	Olive oil	19·83	0·9160	,, ,,
9	Olive oil	23·78	0·9147	,, ,,
10	Olive oil, from bagasse . . .	71·12	0·9277	Klein[3]
11	Sulphur olive oil, Italian . . .	48·2	0·9197	Lewkowitsch[4]
12	Sulphur olive oil, Italian . . .	49·4	0·9204	,,
13	Sulphur olive oil, Syrian . . .	64·2	0·9193	,,
14	Olive oil, Californian . . .	12·11	0·9149	Tolman and Munson[5]

In order to remove the uncertainty attaching to the determination of the specific gravity of oils containing free fatty acids, *Archbutt* proposed to take the specific gravities of the liberated fatty acids. Most fatty acids being solid at the standard temperature, the determination should be made at the boiling point of water, but the meagre information so obtained will hardly repay the trouble entailed (cp. Chap. VIII. and Vol. II. Chap. XIV.).

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[1] Cp. A. O. Ransome, *Journ. Soc. Chem. Ind.*, 1912, 672.

[2] *Journ. Soc. Chem. Ind.*, 1890, 589.

[3] *Ibid.*, 1898, 1055.

[4] Unpublished notes.

[5] *Journ. Amer. Chem. Soc.*, 1903, 957. The average specific gravity of Californian oils was found to be 0·9168.

The changes in specific gravity which are brought about by oxidation are indicated in the following table due to *Thomson and Ballantyne*;[1] the oils were exposed to the action of direct sunlight in uncorked bottles, the contents being shaken up every morning for six months :—

Kind of Oil.	Specific Gravity at 15·5° C. (Water at 15·5° C.=1.)						
	Original.	After 1 Month.	After 2 Months.	After 3 Months.	After 4 Months.	After 5 Months.	After 6 Months.
Olive . . .	0·9168	0·9187	0·9193	0·9208	0·9215	0·9227	0·9246
Castor . . .	0·9679	0·9681	0·9691	0·9700	0·9700	0·9685	0·9683
Colza . . .	0·9168	0·9183	0·9172	0·9185	0·9184	0·9200	0·9207
Cotton seed .	0·9225	0·9237	0·9241	0·9261	0·9278	0·9304	0·9320
Arachis . .	0·9209	0·9213	0·9221	0·9233	0·9239	0·9256	0·9267
Linseed . .	0·9325	0·9331	0·9336	0·9353	0·9359	0·9372	0·9385

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[1] *Journ. Soc. Chem. Ind.*, 1891, 30. Cp. also Sherman and Falk, *Journ. Amer. Chem. Soc.*, 1903, 711.

2. Melting and Solidifying Points

The several methods proposed hitherto for the determination of the **melting points** of fats, unfortunately lead to discordant results. Nor is this to be wondered at if we remember that natural oils and fats are not definite chemical substances, characterised by a definite melting point, but are mixtures of a number of glycerides. A further complication arises from the fact that even pure glycerides, such as trimyristin, tripalmitin, and tristearin, present in their melting points irregularities such as are not shown, as a rule, by definite chemical substances. It has been explained above that even pure triglycerides have two melting points, and that the true melting point (the higher one) is only obtained with crystallised glycerides. The conflicting views as to the true explanation of the so-called double melting points have been detailed in Chap. I. p. 21. But whatever the correct explanation, it is obviously desirable that before determining the melting point of even a pure glyceride, endeavours should be directed to obtaining it in a crystalline condition.

As stated above, *Bömer* termed the first melting point "transition point." The manner in which this "transition point" is determined in the case of a pure glyceride will be described in Chap. XII.

In the case of commercial oils and fats it is, as a rule, impossible to obtain the crystalline form. Hence the specimens subjected to examination do not melt sharply at a definite degree of temperature, but soften first, and only melt to a clear liquid after further heating.

This is due to the fact that most natural oils and fats consist to the largest extent of mixed glycerides, the melting point of which must obviously lie below the melting point of mixtures of true tripalmitin, tristearin, and triolein. Such mixtures have been prepared and examined by *R. Kremann and R. Schoulz* [1]; the most important of their results are reproduced in the following tables :—

Melting Points of Mixtures of Tripalmitin and Tristearin

Tripalmitin.	Tristearin.	Temperature.
Per cent.	Per cent.	° C.
0·0	100·0	56·0 [2]
10·0	90·0	60·4
12·0	88·0	60·1
25·0	75·0	58·0
30·6	69·4	57·8
39·8	60·2	56·0
47·0	53·0	57·2
50·0	50·0	56·2
56·2	43·8	55·1
68·8	31·2	54·5
91·6	8·4	60·4
100·0	0·0	62·6

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[1] *Monatsh. f. Chem.*, 1912 (33), 1063.

[2] It will be seen from p. 27 that the melting point of pure tristearin is 71° C. The temperature given by R. Kremann and R. Schoulz evidently refers to the "transition point."

Melting Points of Mixtures of Tristearin and Triolein

Tristearin.	Triolein.	Temperature.
Per cent.	Per cent.	° C.
0·0	100·0	– 7·0
4·8	95·2	+28·0
14·7	85·3	44·0
23·3	76·7	50·7
31·2	68·8	56·0
52·8	47·2	64·3
74·6	25·4	64·3
100·0	0·0	56·0

Melting Points of Mixtures of Tripalmitin and Triolein

Tripalmitin.	Triolein.	Temperature.
Per cent.	Per cent.	° C.
0·0	100·0	– 7·0
6·1	93·9	+25·0
21·5	78·5	48·2
26·1	73·9	50·0
47·0	53·0	56·9
72·8	27·2	60·9
100·0	0·0	62·6

MELTING POINTS OF MIXTURES OF TRISTEARIN, TRIPALMITIN, AND TRIOLEIN

A. *Tristearin and Tripalmitin in the Proportions of* 9 : 1

Tristearin.	Tripalmitin.	Triolein.	Temperature.
Per cent.	Per cent.	Per cent.	° C.
90·0	10·0	0·0	60·4
81·4	9·0	9·6	61·9
62·7	7·0	30·3	64·4
51·9	5·8	42·3	64·2
42·2	4·7	53·1	62·7

B. *Tristearin and Tripalmitin in the Proportions of* 3 : 1

Tristearin.	Tripalmitin.	Triolein.	Temperature.
Per cent.	Per cent.	Per cent.	° C.
75·0	25·0	0·0	58·0
67·0	22·3	10·7	57·0
57·3	19·1	23·6	57·7
47·9	16·0	36·1	56·4
40·7	13·0	46·3	58·5
18·5	6·1	75·4	50·7
13·6	4·5	81·9	47·0
9·5	3·1	87·4	44·2

C. *Tristearin and Tripalmitin in the Proportions of* 1 : 1

Tristearin.	Tripalmitin.	Triolein.	Temperature.
Per cent.	Per cent.	Per cent.	° C.
50·0	50·0	0·0	56·2
45·4	45·4	9·2	56·2
41·1	41·1	17·8	56·0
34·4	34·4	31·2	54·4
29·8	29·8	40·4	52·0
26·5	26·5	47·0	52·0
23·4	23·4	53·2	50·0
15·0	15·0	70·0	44·7
10·5	10·5	79·0	42·8
4·5	4·5	91·0	31·7
0·0	0·0	100·0	7·0

D. *Tristearin and Tripalmitin in the Proportions of* 1 : 3

Tristearin.	Tripalmitin.	Triolein.	Temperature.
Per cent.	Per cent.	Per cent.	° C.
25·0	75·0	0·0	. .
6·3	18·9	74·8	39·9
4·0	11·9	84·1	36·2

For tables giving the melting points of mixtures of tripalmitin, tristearin, and triolein in other proportions, the original paper must be consulted.

The melting points of mixtures of a pure simple triglyceride and a pure mixed triglyceride are given in the following table :—

Melting Points of Mixtures of Tristearin and α-Palmito-β-γ-Distearin (Limprich [1])

Tristearin from Mutton Tallow.	α-Palmito-β-γ-Distearin.	Melting Point of Glycerides			Melting Point of the isolated Fatty Acids.
		Crystallised from Solution.	Transition Point.		
		° C.	° C.	° C.	° C.
100	...	72·1	54·8	73·0	69·4
90	10	71·5	54·2	71·1	68·6
80	20	70·6	54·0	70·2	67·6
70	30	69·5	53·5	69·3	67·3
60	40	68·3	53·0	68·2	66·6
50	50	67·4	52·8	67·2	66·0
40	60	65·8	52·5	65·8	65·4
30	70	64·7	52·0	63·4	64·8
20	80	64·5	51·8	64·2	64·0
10	90	66·2	51·6	66·2	63·4
...	100	67·8	51·1	67·7	62·4

There is also much uncertainty as to which of the two temperatures should be taken as the melting point, the one at which a fat commences to liquefy, or the one at which it becomes perfectly transparent. Some experimenters identify the melting point with that temperature at which the fat undergoes a certain degree of softening, either sufficient to permit a plug of fat, contained in a glass tube (either a capillary tube or a tube of 5 to 7 mm. diameter) open at both ends, to be forced up by the hydrostatic pressure of water (*Bouis*), or sufficient to allow the fat to form a globule (*Wimmel*). A further difficulty is caused by the fact that some fats—lard, tallow—become transparent at a temperature which lies several degrees above that at which they liquefy completely. The reverse behaviour is shown by Japan wax.

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[1] *Inaug. Dissert.*, Münster, i/W, 1912.

The want of a uniform method for the determination of the melting point is therefore much felt, and one that would command general acceptance is still a desideratum, as in the valuation of some commercial fats (such as chocolate fats) considerable importance attaches to the melting point.

It should be borne in mind that fats do not exhibit their normal melting point shortly after being melted. It is only recovered after the lapse of a day or two; therefore if a sample has been melted, it should be allowed to stand some time (at least over night) before its melting point is determined.[1]

On the Continent *Pohl's* method is largely employed. According to this method the temperature is ascertained at which the fat is just becoming liquid, although it may still retain solid particles. The globular bulb of a mercury thermometer is immersed in the melted fat and quickly removed, so that only a thin coating of fat adheres to it. After a day or two the thermometer is fixed, by means of a cork, in a long and wide test-tube, in such a manner that the bulb is still at a distance of about half an inch from the bottom. The test-tube is then fastened in a clamp and gently warmed by the heat radiating from a heated sheet of iron or asbestos placed below it at a distance of about one inch. The temperature is allowed to rise only very gradually. At the moment when a drop of liquid fat is observed to form at the bottom of the bulb, the temperature is read off; this is recorded as the melting point.

Some of the inaccuracies which attach to this procedure were removed by *Finkener*, who coats glass rods of specified dimensions with the fat; but even then it is impossible to obtain a homogeneous coating.

More precision has been given to *Pohl's* method by *Ubbelohde*,[2] who provides the bulb of a thermometer with a metal casing in which a small open glass vessel (cap), having a hole at the bottom, can be fitted tightly. The fat to be examined is pressed into the glass vessel, which is then slipped into the metal casing, so that the bulb of the thermometer is embedded in the fat. The thermometer is then placed in a long and wide test-tube, which is immersed in a water-bath. By slowly raising the temperature of the water-bath, the "softening point," *i.e.* the point at which the fat just commences to protrude through the hole in the bottom of the glass cap, as also the "dropping point," *i.e.* the degree of temperature at which the melted fat drops off, can be observed. The author has found *Ubbelohde's* contrivance useful in the examination of lubricating greases melting below 100° C. In the case of solid fats the same results were obtained as by *T. Redwood's*[1] slightly modified form of *Pohl's* method :—A minute quantity of the melted fat, nearly cooled to its solidifying point, is placed, by means of a thin glass rod, on clean mercury contained in a small dish and allowed to solidify. The dish may be placed in a beaker containing water, which is heated gradually. A thermometer is dipped in the mercury, and that temperature at which the fat spreads over the mercury is recorded as the melting point. This method can be recommended ; it is, however, preferable to place a somewhat large quantity of the not previously melted fat on the surface of the mercury.

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[1] Cp. Vol. II. Chap. XIV. "Cacao Butter."

[2] *Zeits. f. angew. Chem.*, 1905, 1220.

Frequently the melting point is ascertained in capillary tubes closed at one end, such as are employed for determining the melting points of pure organic substances.[2] The "Society of Bavarian Analytical Chemists" agreed upon the following *modus operandi* :—Draw a column of fat, 1 to 2 cm. high, into a thin-walled capillary tube ; seal one end of the tube, and attach the latter to the stem of a thermometer in such a manner that the substance and the mercury bulb are at the same level. After an interval of about twenty-four hours immerse the thermometer in glycerin contained in a test-tube about an inch and a half wide, and heat the liquid very gently. The temperature at which the thin cylinder of fat has become perfectly clear and transparent is considered to be the melting point.

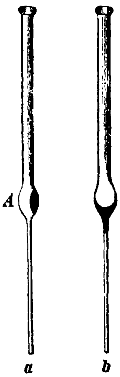

Fig. 14.

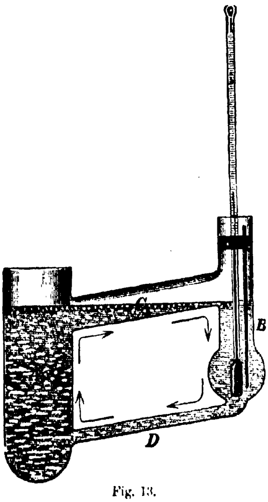

Fig. 13.

An apparatus adapted for this method was designed by *Olberg* ; it is shown in Fig. 13. The vessel is filled with oil, and on heating at *A* circulation takes place spontaneously without any stirring being required[3] in the direction C, B, D.

The capillary tubes must not be chosen too narrow. Unless attention be paid to this point, differences amounting to several degrees may be found between the results obtained by determining the melting point on mercury and in capillary tubes, the differences increasing as the diameter of the capillary decreases. The determination of the melting point of fats in capillary tubes must therefore be made with due caution. The uncertainty attaching to the determination of the melting point in capillary tubes led *Bensemann* [1] to fix upon two points, viz. the point of *incipient fusion* and the point of *complete fusion*. This method is still largely used on the Continent. A drop of the melted fat is placed in a tube as shown in Fig. 14, *a*, and allowed to solidify in such a position that it forms a globule at A. The tube is then attached to a thermometer and immersed in water contained in a beaker. By gently warming the water over a very small flame a point is reached when the fat just begins to flow down the side of the tube. The temperature at which this takes place is recorded as the "point of incipient fusion." The drop of fat will then occupy the position shown in *b*. By further application of heat, the drop becomes completely transparent; the corresponding temperature is the "point of complete fusion." The difference between these two points is about 3° to 4° C.

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[1] *Analyst*, 1877, 51.

[2] Cp. T. Tyrer and A. Levy, *Pharm. Journ.*, 1899, July 29 ; cp. also Wegscheider, *Chem. Zeit.*, 1905, 1225.

[3] Cp. also Thiele, *Berichte*, 1907, 996.

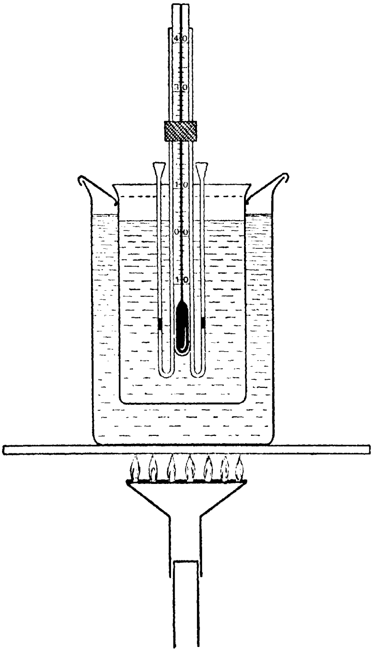

Fig. 15.

A more convenient form of melting point tube, proposed by *Bömer*,[2] is shown in Fig. 15. In the United States of America *Wiley's* official method [3] is frequently used.

Several chemists proposed an acoustical method for ascertaining the melting point of fats. The principle on which apparatus of this kind is based is the following: Two platinum wires connected to a battery and an electrical bell are immersed in the solid fat. On the latter becoming melted the circuit is closed, and the bell rings. The first apparatus of this kind was designed by *Loewe*, and was modified in some minor points by *Jean*. The essential part of *Jean's* apparatus consists of a U-tube, into which is poured a quantity of the melted fat, sufficient to fill the bend of the tube. Platinum wires are then introduced into the solidified fat down each limb of the tube, and connected with a battery and an electric bell. Next a little mercury is poured into one of the limbs of the tube, which is placed in a water-bath. When the fat melts, the mercury falling through it, closes the circuit.

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[1] *Journ. Soc. Chem. Ind.*, 1885, 534.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (xvii.), 363.

[3] *Official and Provisional Methods of Analysis*, Assoc. of Agricult. Chemists, 1907, 133; cp. also G. A. Menge, "A Study of Melting-Point Determinations," *Hygienic Laboratory*, Bulletin No. 170, Washington, 1910; H. Steenbock, *Journ. Ind. and Eng. Chem.*, 1910 (2), 480.

Another apparatus of the same type has been designed by *Christomanos*.[1] It is shown in Fig. 16.

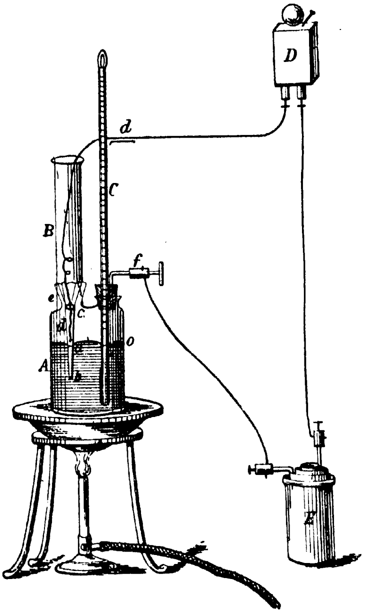

Fig. 16.

The acoustical methods entail too much trouble for commercial work; in view of the small amount of information that is gained, even from a correct melting point, they must be considered an over-elaboration of a method which should only be resorted to in exceptional cases.

Le Sueur and Crossley[2] proposed to determine the melting point in the following manner: Place in a thin-walled tube, about 75 mm. long and 7 mm. wide, a fine capillary tube, open at both ends, and protruding over the thin-walled tube. The diameter of the capillary should not exceed ¾ mm. A small portion of the fat under examination is then introduced into the thin-walled tube, so as to cover the lower part of the capillary. The whole is then attached to the stem of a thermometer (by means of india-rubber bands) and placed in a beaker containing the heating fluid. The temperature at which the liquid is seen to rise in the capillary tube is noted as the melting point of the fat. Whereas this method gives accurate results in the case of pure chemical substances, it did not give in my laboratory reliable results with fats. Two defects are inherent to this method. The one is the tendency to give too low a melting point in the case of fats containing glycerides of lower fatty acids (such as butter fat and cocoa nut oil) owing to a portion of the fat having liquefied and risen in the capillary tube, whilst the remainder had not yet melted. The second error is due to the viscosity of fats; this plays an important part in such cases as tallow, wool fat, and chocolate fats; hence the melting points are found too high.

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[1] *Journ. Soc. Chem. Ind.*, 1890, 894; cp. also Limbourg, *Bull. Soc. Chim. Belgique*, 1908, 117; L. v. Liebermann, *Zeits. f. Unters. Nahrgs- u. Genussm.*, 1911, xxii. 294.

[2] *Journ. Soc. Chem. Ind.*, 1898, 988.

The following table reproduces some results obtained in my laboratory by various methods:—

Comparative Determinations of Melting Points of some Fatty Substances (Lewkowitsch)

Fat.	Le Sueur and Crossley's Method.			Ordinary Capillary-tube Method.	Hydrostatic Pressure Method.	Mercury Method.
	Softens in Outer Tube at	Clear in Outer Tube at	Rises in Capillary Tube at			
	°C.	°C.	°C.	°C.	°C.	
Wool fat . . .	...	...	45·6	36·7-39·2	32·4	
			45·6	36·5-39·2		
			45·6			
	32	40	45·7	37·1-39·8	30·2-31·8	
			45·4	37·4-39·8		
			45·7			
Butter fat . .	...	36	25·7-25·8	32·0-33·4		
			25·7-25·8	32·0-33·45		
Cocoa nut oil . .	...	26	22·8	24·8-25·2		
			23·2	24·8-25·2		
Stearolactone . .	...	39·1	34·8	37·0-37·7		
Tallow . . .	...	...	45·4	41·1-45·0		
Oleomargarine . .	...	...	...	25·5		uncertain[1]
"Chocolate fat"—I.	...	...	34·4	28·3-28·9		31
"Chocolate fat"—II.	...	...	35·5	28·3-28·9		
"Chocolate fat"—III.	...	...	...	25		26·6
"Chocolate fat"—IV.	..	...	...	32	35	35-37
"Chocolate fat"—V.	...	...	...	36·1	35	34-36

It will be seen from the preceding remarks that the exact determination of the melting point of a fat is attended with difficulties; moreover, the drawback attaches that some time must be allowed to elapse before a sample can be tested.

For purposes of discrimination between various oils, the melting point has, as a rule, little analytical value. It is therefore unnecessary to add here tables enumerating the melting points of oils. In special instances, however, such as in the valuation of "winter oils," the melting point is of considerable importance.

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[1] Commenced to melt at the edges at 25° C.; about half of the lump melted at 30° C., and melted completely at 37·8° C.

Of greater importance is the determination of the melting point of solid fats, as it is frequently required to value different specimens of one and the same kind of fat on the basis of their melting points. As has been explained above, the methods in vogue yield different results. An agreement between analytical chemists as to an exact method is desirable. A table in which the various melting points were set out would show so glaring a disagreement between various observers, that I consider it useless to collate the numbers here. The melting points of the natural fats will be found detailed under their respective headings in Vol. II. Chap. XIV.

It should be noted that small amounts of free fatty acids influence the melting point considerably.

Special directions for the determination of the melting points of lard substitutes, paraffin wax, and spermaceti will be found in Vol. III. Chap. XV. under the headings "Lard Substitutes," "Paraffin Wax," and "Sperm Candles."

Less uncertainty attaches to the melting point of the mixed fatty acids derived from an oil or fat; therefore, in examining a sample of fat for commercial purposes, the **melting point of the free fatty acids** is usually taken. (For the method employed for this purpose see Chap. VIII.)

When melted substances **solidify**, the "latent heat of fusion" is liberated and a rise of temperature takes place. Whereas fatty acids show this rise most distinctly, it is not so well marked in the case of fats, although if large quantities be taken, the rise of temperature can be observed distinctly (cp. Vol. II. Chap. XIV. "Lard"). Fats are rather characterised by the feature that the temperature remains constant for some time before falling further.

It should be distinctly understood that these and the following notes only refer to natural fats. "Hardened Fats" (see Vol. III. Chap. XV.) show, or may show, a different behaviour which has not been studied hitherto.

Rüdorff studied the **solidifying points**, with a view to their application as characteristics in the examination of fats. His method was to melt a fat and to agitate it continuously with a thermometer, noting the temperature from time to time. He found that in the case of some fats the temperature fell to a certain point, remained constant thereat for a time, and then fell again. During the period of constant temperature the fat solidified; this temperature he judged to be the solidifying point.

Again, in the case of other fats, on solidification setting in, a fall of temperature takes place with a subsequent rise, until a maximum is reached, and then the temperature remains constant until the mass has become solid throughout.

A number of other fats, such as beef and mutton tallow, exhibit no solidifying point proper, the temperature rising a few degrees, but not remaining constant for any length of time. These fats behave like mixtures (which indeed they are, see Vol. II. Chap. XIV.), part of which has become solid whilst the remainder is still liquid.

The author does not, therefore, recommend to determine the solidifying point of fats, but rather determine the solidifying points of their **fatty acids** (see Chap. VIII.).

A number of solidifying points observed with commercial lards will be found under "Lard" in Vol. II. Chap. XIV.

Polenske[1] pointed out that the difference between the melting and solidifying points of specimens of one and the same kind of animal fat is nearly constant, whereas it varies for animal fats of different origin. This is brought out clearly by the data given in the following table, in which a few "differences" of some animal and also of vegetable fats are recorded :—

Kind of Fat.	No. of Specimens.	I. Melting Point. ° C.	II. Solidifying Point. ° C.	III. Difference. I.-II.
Tallow stearine .	2	54·2 ; 56	41·5 ; 43·5	12·7 ; 12·5
Tallow . . .	47	41·2-52	28·4-35·4	12·8-15
Lard . . .	15	42·2-49	23-28·4	19·2-20·6
Goose fat . .	6	32·2-38·3	17·5-21·7	14·7-16·7
Butter fat . .	2	34·5 ; 35·5	22·7 ; 21·2	11·8-15·9
Horse fat . .	2	33·0 ; 35·3	18 ; 19	15·0 ; 16·3
Cocoa nut oil [2] .	5	24·5-26·0	19·0-22·5	4·8-6·0
Shea butter .	..	45	25·0	20
Borneo tallow .	..	48·5	40·0	8·5

For the details of the apparatus, and the manner in which *Polenske* determines the melting point, the reader must be referred to the original papers. It need, therefore, only be pointed out that *Polenske* proposes to detect, with the help of the "difference number" (as he terms the numbers given in the last column of the preceding table), admixtures of one animal fat to another, such as lard and beef fat to goose fat, etc. (see Vol. II. Chap. XIV.). It is, however, absolutely essential to follow minutely the *modus operandi* prescribed by *Polenske*.

It will be observed that the differences in the case of cocoa nut oil and Borneo tallow are comparatively small, whereas in the case of shea butter the difference is higher than in the case of animal fats. A much more extended series of observations is, however, required before general deductions can be made. This becomes obvious from the fact that in his second paper *Polenske* was forced to raise the "difference numbers" in the case of goose fat and of butter fat.

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[1] *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1907, xxvi. 3, 444 ; 1908, 273.

[2] In the case of a "hardened" cocoa nut oil, having the iodine value of about 1, the "difference number" had risen from 5·2 to 16·8, the melting and solidifying points respectively of original and "hardened" cocoa nut oils having been raised from 25·6 and 20·4 to 44·5 and 27·7.

Fischer and Alpers[1] state that *Polenske's* limits must be widened, and whilst the method may be useful for the detection of considerable quantities of tallow in lard, it is useless for the detection of foreign animal fats in butter fat (cp. *Bömer and Limprich*[1]).

The following observation may also prove useful. It has frequently been noticed that a mixture of oleostearine and cotton seed oil of a definite "titer test" (see Chap. VIII.) crystallises at a much higher temperature than a mixture of pure lards of the same titer test. It has also been noticed that a mixture of lard oil and lard stearine crystallises at a much higher temperature than a corresponding mixture of lard oil and oleostearine.[2]

The **solidifying or freezing (congealing) point of oils** is determined with the aid of freezing mixtures, in which tubes containing the oil are placed. The thermometer is inserted in the tube by means of a cork; it is convenient to use a thermometer, the scale of which commences above the cork. The following table[3] gives the proportions of water and certain salts required for the preparation of some freezing mixtures:—

Substances used.	Parts per 100 of Water.	Temperature obtained. ° C.
Distilled water . . .		0
Potassium nitrate . . .	13	−2·85
Potassium nitrate . . .	13	−5·0
Sodium chloride . . .	3·3	
Barium chloride . . .	35·8	−8·7
Ammonium chloride . .	25·0	−15·4

If snow is available, lower temperatures can be obtained, as will be seen from the following table:—

	Substances used per 100 parts of Snow.	Temp. obtained. ° C.
13·5	parts potassium nitrate and 26 parts ammonium chloride .	−17·8
33	parts sodium chloride	−21·3
52	parts ammonium nitrate and 55 parts sodium nitrate .	−25·8
9	parts potassium nitrate and 67 parts ammonium rhodanate .	−28·2
13	parts ammonium chloride and 37·5 parts sodium nitrate .	−30·7
32	parts potassium nitrate and 59 parts ammonium rhodanate .	−30·6
2	parts potassium nitrate and 112 parts potassium rhodanate .	−34·1
39·5	parts ammonium rhodanate and 54·5 parts sodium rhodanate	−37·4
143	parts crystallised calcium chloride ($CaCl_2 + 2H_2O$) . .	−50·0[4]

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 181; cp. also Fritzsche, *ibid.*, 1909, xvii. 532, and Laband, *ibid.*, 1909, xviii. 289. For the "theoretical basis of Polenske's method" cp. A. Bömer and R. Limprich, *ibid.*, 1913, xxv. 367.

[2] Wesson and Lane are of the opinion that this is due to the hard portions of the beef fat, which comprise the bulk of oleostearine, being less soluble in cotton seed oil and in lard at low temperatures, than are the solid portions of hog fat.

[3] *Journ. Soc. Chem. Ind.*, 1889, 423.

[4] J. Duclaux (*Compt. rend.*, 1910 (151), 715) uses a mixture of carbon bisulphide and acetone, thus obtaining a temperature of −48° C.

The freezing point of fatty oils is not characteristic enough for purposes of classification or identification. This determination is therefore resorted to for purposes of valuation, as in the examination of different specimens of neats' foot oil (see Vol. II. Chap. XIV.), "winter oils," and lubricating oils. Elaborate methods for testing lubricating oils have been worked out by the officials of the Königliche Technische Versuchsanstalten, Berlin. Fig. 17 illustrates the apparatus in which the determination of the freezing point of fatty oils is carried out (cp. "Cold Test," Vol. III. Chap. XV.[1]).

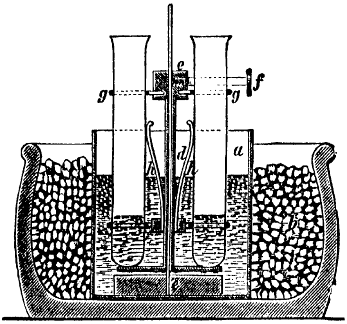

Fig. 17.

3. Refractive Index

The ease and rapidity with which the refractive index can now be determined has given prominence to the refractometric method of examining oils and fats. This method does not afford a perfectly reliable means of detecting adulteration; yet, in many cases, it can be

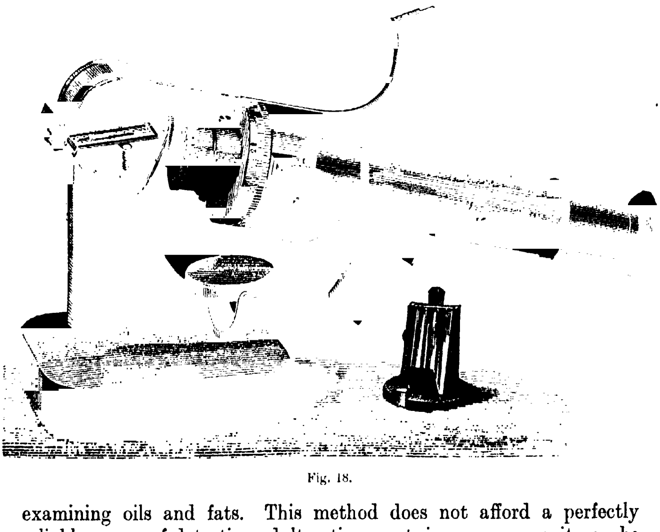

Fig. 18.

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[1] Cp. also A. Loewensteen and L. Boelio, *Eighth International Congress of Applied Chemistry*, 1912, vol. xi. 17.

used as a sorting test, permitting to decide rapidly whether adulteration may be suspected, or whether a genuine sample is under examination (cp. Vol. II. Chap. XIV. " Butter Fat "). The objection of earlier observers, viz. that the refractive index is greatly influenced by the methods of refining, the age of the oil, the amount of free fatty acids, and the amount of oxidation a specimen has undergone, are unfounded to a great extent, more recent researches having proved that very valuable indications (especially in the case of butter fat) can be gained from the determination of the refractive index.

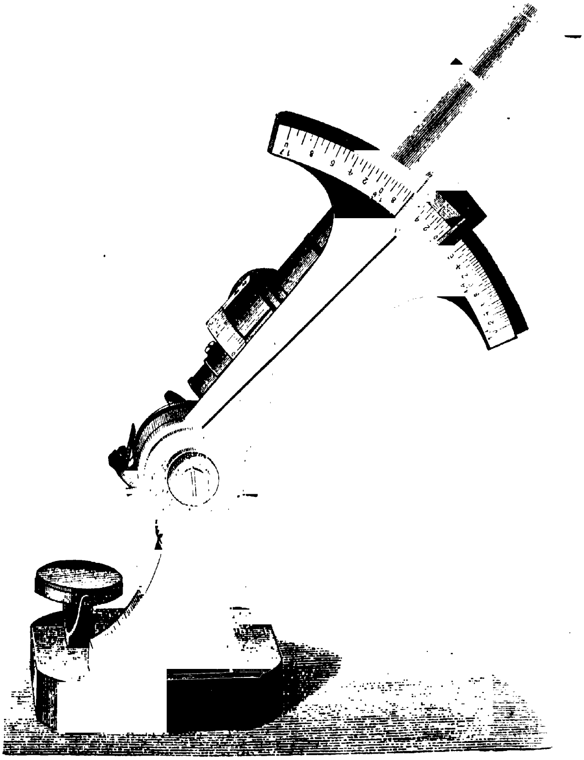

Fig. 19.

In *Abbe's* refractometer the index of refraction is found by observing the total reflection which a very thin stratum of a liquid placed between prisms of a more highly refracting substance produces in transmitted light.[1] A single drop of a fluid is therefore sufficient for the examination, so that fluids which are opaque in a thick layer may be readily examined.

The instrument[2] is shown in Figs. 18 and 19. The former illustrates its position when the drop of fat under examination is applied; the latter shows that position of the instrument in which the readings are taken. The instrument consists of a double prism of highly refracting flint glass (Fig. 18) fixed to an alhidade in such a manner that it can turn round the centre of a divided arc. This arc has fastened to it a telescope turning with it on a horizontal pin. The elongated part of the telescope fits in a support carrying two revolving *Amici* prisms. This system acts as a compensator for achromatising the critical line of total reflection, the amount of rotation being indicated by a divided drum. The drop of liquid to be examined is brought between the two prisms, one of which can be easily removed as shown. In order to make this prism easily accessible, the telescope with the arc can be turned down.

The examination may be made with diffused daylight or with lamplight, and consists in a single adjustment of the alhidade. The refractive index is read directly off the divided arc to the third decimal, so that no calculation is required. The fourth decimal may be estimated accurately within two units.

Zeiss's butyro-refractometer (for the examination of butter) (Fig. 20) has almost completely superseded *Abbe's* refractometer in laboratory practice. Only when the refractive indices of an oil lie outside the range of the butyro-refractometer, as in the case of tung oil and rosin oils, the *Abbe* refractometer is required. The butyro-refractometer differs from the *Abbe* instrument in that the critical line of total reflection for a given substance—in this case butter fat—is achromatised, not by a special compensating arrangement, but by the refractometer prisms themselves, the dispersion co-existent with the total reflection between glass and substance being exactly compensated by the dispersion due to the surface when the light emerges from the double prism in the direction of the telescope. Accordingly, the critical line appears colourless (achromatised) for the standard substance for which the prisms have been calculated, whilst all substances differing from it in refractive and dispersive power cause the critical line to appear more or less blue when the dispersion is higher, or red when it is lower than that of the standard substance. The critical line is, however, in all cases sufficiently distinct to admit of its exact position being ascertained. In the latest instruments the refractometer is provided with a micrometer screw which permits of greater accuracy in reading, as the dividing line can thereby be shifted in either direction by one whole degree, so that the uncertainty in gauging tenths of degrees is removed to a great extent.[3] Thus two different substances are, in the first instance, distinguished by the different positions of the critical line, and next by the difference in appearance as regards a coloured fringe. Since the prisms of the butyro-refractometer are calculated for pure butter fat, the presence of foreign fats in a sample of butter fat can in many cases be detected by a simple examination under this instrument.[1]

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[1] E. Abbe, *Neue Apparate zur Bestimmung des Brechungs- und Zerstreuungsvermögens fester und flüssiger Körper.* Jena, 1874.

[2] Made by Carl Zeiss, Optische Werkstätte.

[3] F. Loewe, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 15.

To make an observation, place the instrument upon a table, where diffused daylight or any form of artificial light can be readily admitted for illumination. Supply through nozzle D a stream of water of constant temperature.[2] Then open the prism casing by giving to pin F about half a turn to the right, until it meets with a stop, and turn the half B (held in position by H) of the casing aside. The prism surfaces must now be cleaned with the greatest care; this is best done by applying soft linen moistened with a little alcohol or ether. Then pour a few drops of the clear (filtered) fat on to the surface of the prism contained in casing B. For this purpose the apparatus should be raised with the left hand, so as to place the prism surface in a horizontal position.

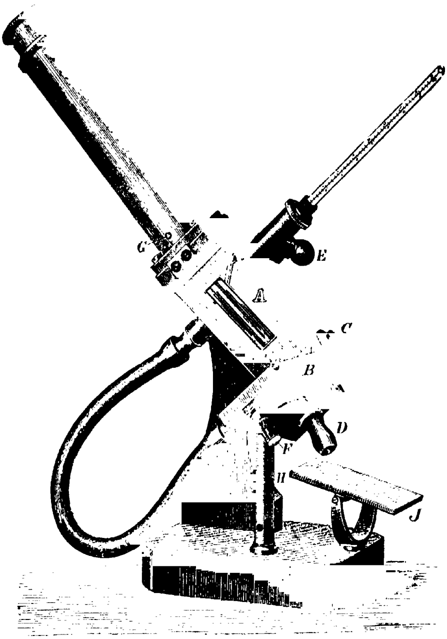

Fig. 20.

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[1] For the theory underlying the construction of the butyro-refractometer cp. also Baumert, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 135.

[2] Cp. Fig. 26, p. 334.

Then press B against A, and bring F back into its original position by turning it in the opposite direction.

While looking into the telescope, give the mirror J such a position as to render the critical line, which separates the bright left part of the field from the dark right part, distinctly visible. If the space between the prisms is not filled completely with the sample, the critical line will not appear distinct. Finally adjust the movable part of the telescope, so as to focus the scale.

The critical line, somewhat hazy at first, approaches a fixed position after a short time and quickly attains its greatest distinctness. This point being reached, the reading of the thermometer [1] is taken, unless a definite temperature has been arranged for at the outset. The adjustment of the instrument should be tested periodically by means of a *standard fluid* (supplied with the instrument), the critical line of which must occupy a definite position on the scale. With the aid of a watch-key inserted in G, the position of the objective can be altered at will.

The scale divisions are converted into refractive indices by reference to the following table :—

Table of Refractive Indices

Scale Division.	n_D.	Difference.
0	1·4220	
10	1·4300	8·0
20	1·4377	7·7
30	1·4452	7·5
40	1·4524	7·2
50	1·4593	6·9
60	1·4659	6·6
70	1·4723	6·4
80	1·4783	6·0
90	1·4840	5·7
100	1·4895	5·5

Pulfrich's [2] refractometer is also provided with a special arrangement for observations at somewhat elevated temperatures. This refractometer [3] is shown in Fig. 21. The observations are made with sodium light, placed opposite the reflecting prism N, or with hydrogen light, emanating from the Geissler tube Q. The sodium light is thrown by means of the reflecting prism N, and the hydrogen light by means of the condenser P, on to the substance under examination. (The illumination can be changed rapidly from one source of light to the other by displacing N.) The substance is placed direct on to the surface of the refractometer prism in the manner illustrated by Fig. 22, and the prism, together with the substance, can be brought to any desired temperature in a special heating apparatus S (Fig. 23), by allowing the heating liquid to flow in the direction indicated by the arrows. The piece of wood *W* (Fig. 21) serves to prevent loss of heat.

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[1] Special thermometers are supplied by the makers of the butyro-refractometer for examination of lards and butter fats, which show at a glance deviations from *assumed* normal values of these fats. The author has not admitted the "differential values" into this work.

[2] C. Pulfrich, *Das Totalreflectometer und das Refractometer für Chemiker*, etc., Leipzig, 1890.

[3] Made by Carl Zeiss, Optische Werkstätte, Jena.

The light falling into the substance to be examined under grazing incidence passes through the vertical face of the 90° prism, and the angle *i* at which the limiting ray emerges from the vertical face is read off by means of a telescope and graduated circle. The refractive index *n* of the substance is calculated by means of the formula $n = \sqrt{N^2 - \sin^2 i}$, where N is the (known) refractive index of the prism.

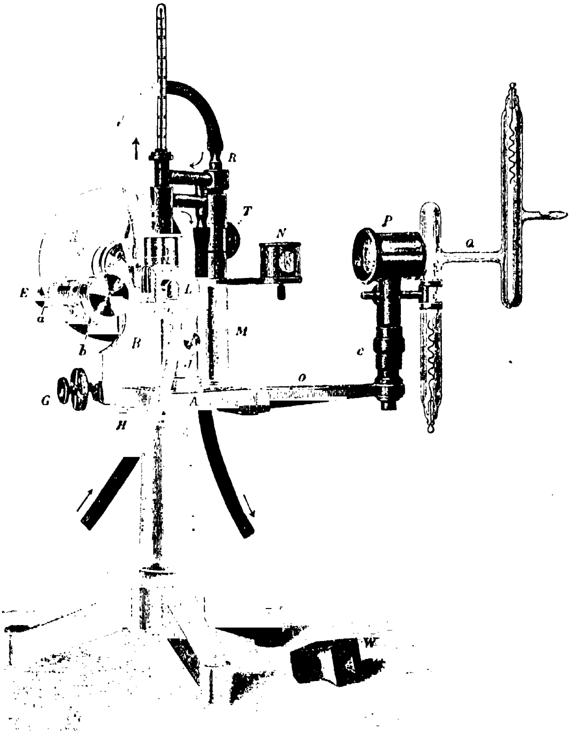

Fig. 21.

For the convenient supply of water to the butyro-refractometer at a constant temperature and under constant pressure, a water-pressure regulator (Fig. 24), consisting of the two vessels A and B, may be used in conjunction with a thermostat[1] (Fig. 25). The butyro-refractometer is inserted between the thermostat and vessel B.

A combination of the *Abbe* refractometer with the heating apparatus of the butyro-refractometer—necessary for the determination of the refractive indices of such oils as tung oil and rosin oils (see p. 337)—at a constant temperature is shown in Fig. 26.

A type of instrument based on an arbitrary scale was constructed in France, before the butyro-refractometer appeared on the market, by *Amagat and Jean* for the examination of oils and fats, and especially of butter fat. The apparatus, termed by its designers oleo-refractometer (Fig. 27), consists essentially of a collimator, a telescope, and a metallic vessel. The latter is fitted with parallel plate-glass sides, and its relative position to the collimator and telescope is fixed in such a manner that a ray of light entering through the collimator must pass through the plate-glass sides and the telescope. In the centre of the metallic vessel a small hollow silver cylinder A having two plate-glass ends is inserted, so arranged as to form an angle of 107°. The telescope

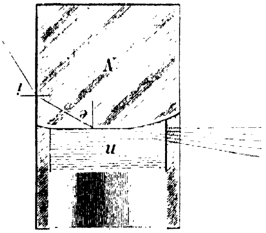

Fig. 22.

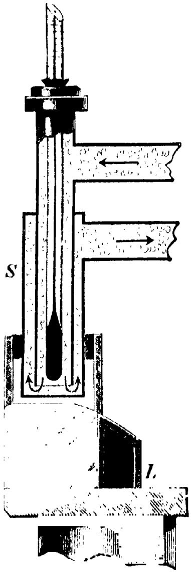

Fig. 23.

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[1] A somewhat more convenient thermostat, occupying less space, is recommended by T. E. Thorpe, *Journ. Chem. Soc.*, 1904, 257; cp. also von Heygendorff, *Chem. Zeit.*, 1909, 244; Poda, *ibid.*, 1910, 1882; Ch. A. Hackman, *Chem. News*, 1910, 192.

is furnished with an arbitrary glass scale, H, placed in the focus of the eye-piece, M, on which is thrown the image produced by a semicircular stop inserted in the collimator, thus dividing the field into a dark and a light portion. If the silver cylinder and the outer circular vessel be filled with the same oil, there will be no refraction, and consequently no alteration in the position of the image. If, however, the inner silver cylinder be filled with a different oil, the light will be refracted, the amount of refraction depending on the nature of the oil; consequently the line dividing the field will be displaced to the right or left. The amount of displacement is read off the scale of the telescope, and is expressed by the number of scale divisions or "degrees."

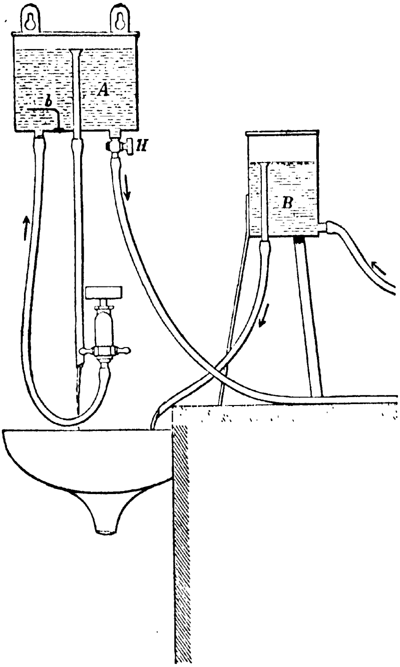

Fig. 24.

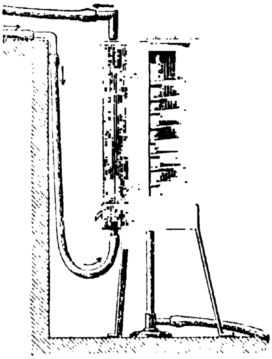

Fig. 25.

For practical use the outer vessel is filled with a standard oil (*huile type*) [the composition of which is, curiously enough, kept secret by the inventors;[1] it is supplied together with the instrument], and the semicircular stop is so adjusted that the line dividing the field into a dark and a light portion falls on the zero point of the scale. The inner cylinder is then filled with the oil under examination, and the displacement of the dividing line, *i.e.* the amount of refraction, is read off. Instead of using the "standard oil," a sample of oil may of course be compared with a specimen known to be pure.

---

[1] The "huile type" is sheep's foot oil.

For the sake of greater convenience in practical use both the cylindrical vessel and the silver cylinder can be emptied (and washed out) by means of taps, only one of which, R, is shown in Fig. 27. A water-jacket (not shown) surrounding the centre part of the instrument allows the temperature of the oil under examination to be regulated. The water in the jacket can be heated by means of a lamp to any desired temperature, which is read off a thermometer.

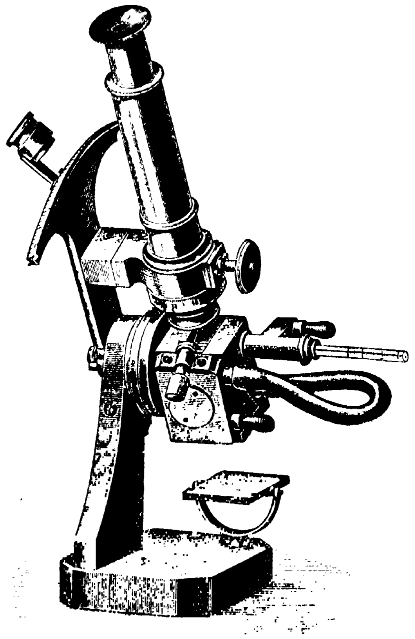

Fig. 26.

Amagat and Jean's oleo-refractometer has this advantage over other refractometers that, being a differential apparatus, it allows of a rapid comparison of two oils under exactly the same conditions.[1]

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[1] Allen (*Analyst*, 1895, 135) points out that the angle of the prism was not strictly the same in all earlier instruments; thus he found for a sample of lard in three instruments 4½°, 6°, and 11° respectively.

The older oleo-refractometers were constructed for the temperature of 22° C., and most of the readings published by earlier observers were taken at this temperature. The instruments placed on the market at present are provided with a double scale for temperatures of 22° C. and 45° C. respectively, so that observations made at 22° C. can be read off at once in the corresponding values at 45° C.

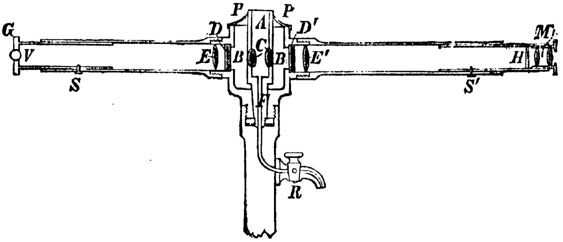

Fig. 27.

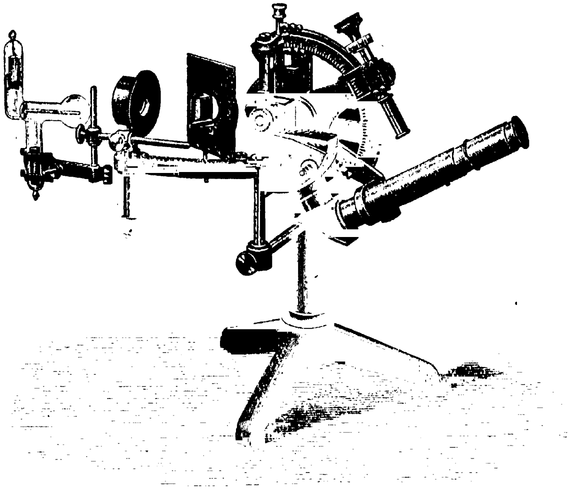

Fig. 28.

A new refractometer (Fig. 28) resembling the *Pulfrich* refractometer has been designed by *Harland*.[1] This instrument differs from *Pulfrich's* refractometer in that essential point that the rectangular prism of the latter is replaced by a cylinder quadrant, made of French flint glass of high refractive power.

[1] Manufactured by Hans Heele, Berlin.

The object to be examined is placed on the polished horizontal surface of the quadrant. The light falls into the substance under grazing incidence, and the limiting ray, after emerging from the cylinder quadrant, passes through a concave cylinder segment (made of the same highly refractive glass as the cylinder quadrant, and of the same radius) in the telescope and thence into the eye of the observer. The angle is read off an arc which is divided into one-quarter degrees (15 minutes); by using the "vernier," single minutes can be read off without difficulty. In order to obtain still greater accuracy, a micrometer screw is provided, the drum of which is divided into 50 divisions. As one total revolution of the drum corresponds to 15′ or 900″, one division corresponds to 18″; this forms the limit of accuracy obtainable with this apparatus. From the observed angle, i, and the known refractive index, N, of the cylinder quadrant, the refractive index, n, of the substance under observation is found with the aid of the formula :—$n = \mathrm{N}.\sin i$.

In order to obviate calculations, there is furnished with the apparatus a table in which the refractive indices, n, are given from 10 to 10 minutes, for all the angles between 34° 44′ 30″ and 87°, for the sodium line D. For any other wave length the refractive index must be calculated; for this purpose the values of N for the rays A′, C, D, F, G′ are given in the table. Thus all refractive indices between 1 and 1·733 can be observed. (For higher refractions it would, of course, be necessary to use a cylinder quadrant, etc., of still higher refractive power.) The instrument is so adjusted that the angle for air is 34° 44′ 30″. This is of great importance, inasmuch as it enables the operator to determine the zero point, as it were, of the instrument at any time.

To observe the refractive index, a sodium light or any other monochromatic light is thrown from a distance of 12 to 16 inches through the rectangular prism on to the object under observation. By turning the rectangular prism downwards and sparking the hydrogen tube provided (see Fig. 28), the refraction for the hydrogen line can be observed, and by thus changing the source of light the dispersion can be measured rapidly, as it is only necessary to turn the micrometer drum, until the dividing line between the dark and the illuminated fields passes again through the centre of the spider web in the telescope.

This dividing line is more sharply defined and is less curved than in other instruments; therefore the angle can be adjusted with greater accuracy than is the case in similar instruments.

In order to make observations at any desired temperature, the quadrant is surrounded with a water-jacket H.

For the observation of liquid substances a trough designed according to the suggestions of the author[1] is provided. In the following table a few observations by the author are contrasted with those obtained in the butyro-refractometer, where applicable. The temperature was 20° C.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1909, 773.

Substance.	Harland's Refractometer.		Butyro-refractometer.	
	Medium used.	Angle observed for D line.	"Degrees."	Calculated.
Water[1] . . .	Wintergreen oil	49° 34′=1·33568	..	..
Tung oil[1] . . .	,,	59° 59′=1·51943	..	..
Soya oil . . .	,,	57° 31′=1·48025	82°	1·4794
Maize oil . . .	,,	57° 15′=1·47683	76°	1·47590
Cottonseed oil . .	,,	57° 20′=1·47721	76°	1·47590
Rape oil . . .	,,	57° 19′=1·47695	76°	1·47590
Arachis oil . . .	,,	57° 4′=1·47278	70°	1·4723
Olive oil . . .	,,	57° 4′=1·47278	70°	1·4723
Castor oil . . .	,,	57° 38′=1·48215	84°	1·4807
Neats foot oil . .	,,	57° 1′=1·47195	67°	1·4705
Cod liver oil . .	,,	57° 38′=1·48215	84°	1·4807
Whale oil . . .	,,	57° 23′=1·47804	77°	1·4765
Thyme oil[1] . . .	,,	58° 45′=1·50017	..	..
Wintergreen oil[1] .	Carbon bisulphide	61° 15′=1·53846	..	..
Rosin oil[1] (containing rosin acids) . .	,,	61° 8′=1·53675	..	..
Rosin oil[1] (free from rosin acids) . .	,,	61° 50′=1·54696	..	..

Other instruments for the refractometric examination of oils have been constructed by *Féry*,[2] by *Leitz*, and by *Eykmann*.

The "immersion-refractometer" constructed by *Zeiss* for the rapid examination of aqueous and alcoholic solutions has been applied to the examination of dilute aqueous solutions of glycerol by *Henkel and Roth*.[3]

The refractive index varies in inverse ratio to the temperature; hence it is necessary that observations be made at a constant temperature. *Tolman and Munson*[4] calculated, from *Procter's*[5] observations, 0·000365 as the correction for each degree Centigrade.[6] According to *Richmond*[7] the factor 0·00038 is more correct. From determinations made with the standard fluid supplied with the butyro-refractometer he derived the following corrections :—

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[1] In this case the butyro-refractometer is useless.

[2] Manufactured by Adam Hilger, Camden Road, London, N.W.

[3] *Zeits. f. angew. Chem.*, 1905, 1940.

[4] *Journ. Amer. Chem. Soc.*, 1902, 754.

[5] *Journ. Soc. Chem. Ind.*, 1898, 1023.

[6] Cp. also Harvey, *Journ. Soc. Chem. Ind.*, 1905, 770.

[7] *Analyst*, 1907, 44. Leach and Lythgo (*Journ. Amer. Chem. Soc.*, 1904, 1193) constructed a sliding scale for reading off the refractive indices corresponding to butyro-refractometer "degrees" at different temperatures. This scale was based upon the factor calculated by Tolman and Munson. Richmond, however, pointed out that the errors in the results obtained by the use of this scale are greater than can be accounted for by the errors of the actual observations. He states that the factor varies with each part of the refractometer scale, and gives a table of the corrections found necessary in the case of a number of fats and oils.

Temp. °C.	Correction for Scale Reading.	Correction for Refractive Index.
15—20	0·62	0·000372
20—25	0·60	0·000372
25—30	0·608	0·000380
30—35	0·615	0·000393
35—40	0·594	0·000386
40—45	0·585	0·000383
45—50	0·583	0·000385

In the butyro-refractometer the correction for butter fat is 0·55 scale divisions ("degrees") for each degree Centigrade; this correction is, however, not applicable to other oils and fats. In order to avoid complications, it is best to make all observations at a definite temperature, to be agreed upon. It is advisable to adopt 40° C. as the standard temperature, most oils and fats being liquid at 40° C., and only in exceptional cases, such as beeswax, higher temperature being required. The temperature should, however, always be stated distinctly.

The presence of free fatty acids in oils and fats appears to affect the refractive index to a marked degree. Thus a sample of Californian olive oil[1] containing 44·4 per cent of free fatty acids, had the refractive index 1·4672, whereas a large number of similar oils containing only small amounts of free fatty acids gave 1·4711.

The following table contains a number of refractive indices observed with the aid of the *Abbe* refractometer, the oleo-refractometer, and the butyro-refractometer respectively. Following the system of classification adopted in this work, they are arranged in the order of the iodine values of the oils, fats, and waxes, so as to show at a glance whether a correlation can be established between the iodine number and the refractive power. No definite relation, however, exists.[2] More complete data will be found in the tables accompanying the description of the individual oils, fats, and waxes in Vol. II. Chap. XIV. It is noteworthy that the oils belonging to the "Terrestrial Animal Oils" deviate in the oleo-refractometer to the left. Too few observations have, however, been made to permit the conclusion that terrestrial animal oils could be readily differentiated from vegetable oils by their behaviour in the oleo-refractometer.

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[1] Tolman and Munson, *Journ. Amer. Chem. Soc.*, 1903, 955.

[2] Cp. E. Durier, *Annal. des Falsific.*, 1909, 489.

[TABLE

Oil.	Class.	Group.	Refractive Index.					
			n_D		Oleo-refractometer.		Butyro-refractometer.	
			°C.		°C.	Degrees.	°C.	Degrees.
Perilla	Drying oils		15	1·4825	...	...	...	...
Linseed			15	1·4835	22	+50 to +54	20	84-90
			60	1·4660	...	...	40	72·5
Tung, Chinese			20	1·5179	22	+75		
Tung, Japanese			20	1·5053				
Candle nut			...	...	...	...	20	78·5
							25	76
Stillingia			23·5	1·4825				
Hemp seed					...	...	35	75
Walnut, Nut			...	...	22	+34 to +37		
Arbutus unedo			...	1·4804	22	+35 to +36	40	64·8
Safflower								
Kaya			16	1·477	...	...	40	65·2
Inukaya			20	1·4758				
Poppy seed			20	1·476				
Soya bean			60	1·4586	22	+30 to +35	40	63·4
Asparagus seed			20	1·4803	...	...	20	82
Amoora			...	...	...	...	25	75
Manihot			...	...	...	...	40	64·5
Melia azedarach			...	...	...	...	40	62·9
Millet seed			...	...	...	...	40	65·1
Niger seed			...	...	...	...	25	70
Sunflower			...	...	22	+26 to +30	40	63·0
Service berry			60	1·4611	22	+35	25	72·2
Argemone			15	1·4753				
Fir seed			...	...	...	...	40	62·5
Strawberry seed			35	1·4769				
Hawthorn seed			25	1·4796				
Currant seed			...	...	...	...	40	67
Mulberry seed			...	...	...	...	40	62
			...	...	...	...	40	63·9
Cameline	Semi-drying oils	Cotton seed oil group	...	...	22	+32		
Pumpkin seed			...	...	...	...	25	70·2-72·5
Maize (corn)			15	1·47665				
			20	1·47625				
Wheat			20	1·48325				
Beech nut					...	...	...	74·5
Kapok			...	...	22	16·5 to 18		
Cotton seed			...	...	...	...	40	51·3
			15	1·4743-1·4752	22	+17 to +23	25	67·6-69·4
Sesamé							40	58·0
			15	1·4748-1·4762	22	+13 to +17	25	68
Luffa seed								
Croton			...	...	...	...	40	62·0
			26	1·4781	22	+35	27	77·5
Mucuna							40	68
Curcas, purging nut			...	...	...	...	25	66·2
			25	1·4681-1·4687	...	...	25	65
Tomato seed							40	56·5
			...	...	...	...	40	63
Spindle tree			...	...	...	...	40	52

Oil.	Class.	Group.	Refractive Index.					
			n_D		Oleo-refractometer.		Butyro-refractometer.	
			°C.		°C.	Degrees.	°C.	Degrees.
Garden cress	Semi-drying oils	Rape oil group	...	...	...	...	40	60·5
Ravison			...	...	22	+18 to +25	20	73-74
Hedge mustard			...	...	...	...	25	70·5-71·5
Rape (colza)			15	1·4720-1·4757	22	+16 to +20	25	68
Black mustard			15·5	1·4672	...	...	40	59·5
White mustard			15·5	1·4750	...	...	40	58·5
Radish seed			...	...	...	...	40	57·5
Jamba			...	...	...	...	25	67·2
Small fennel	Non-drying oils		...	...	...	...	40	58·5
Quince			...	1·4729	...	...	25	68·5
Apricot kernel			20	1·4712	...	...	25	66·6
Plum kernel			...	...	...	...	25	63·1
Peach kernel			...	...	22	+7·5 to +11·5	25	66·1-67·2
Almond			60	1·4555	22	+8 to +10·5	25	64·4
Wheat meal			25	1·4851	...	...	25	92
Acorn			...	1·4731				
Californian nutmeg			...	1·4766				
Arachis			60	1·4545	22	+4 to +7	25	66-67·5
Rice			...	...	...	...	25	68·2
Tea seed			...	...	22	+8		
Tsubaki			20	1·4679-1·4691				
Sasanqua			20	1·4691				
Njore-Njole			22	1·4695				
Pistachio			...	...	...	...	25	62
Hazelnut			...	...	...	...	25	61·2
Koëme			...	...	...	...	25	63·64
							30	61·62
Elderberry			20	1·472				
Olive			15	1·4698-1·4716	22	0 to +3·5	25	62·4
							40	53·5-56·4
Olive kernel			25	1·4682				
Calophyllum			...	...	...	...	40	76
Coffee berry			25	1·4777	...	...	25	79-81·5
Ben			...	...	...	...	40	59
Sterculia			40	1·4654				
Paradise nut			...	...	...	...	15	61·4
Canari			...	...	...	...	40	50·3
Secale			...	...	...	...	25	65
Grape seed		Castor oil group	25	1·4713	...	...	25	69·4
			50	1·4623	...	...	50	54·5
Castor			15	1·4799	22	+39 to +42	25	78
							40	65·5
Menhaden	Marine animal oils	Fish oils	...	...	...	...	25	80·7
							40	71·3
Japanese sardine			20	1·4805	22	+50 to +53	40	58·5
Salmon			...	...	...	...	40	69·5
Pilchard			...	...	...	+32 to +36		

Oil or Fat.	Class.	Group.	Refractive Index.					
			n_D		Oleo-refractometer.		Butyro-refractometer.	
			° C.		° C.	Degrees.	° C.	Degrees.
Cod liver	Marine animal oils	Liver oils	15	1·4800-1·4852	22	+40 to +48	25	75
Shark liver			...	...	22	+29 to +35		
Seal		Blubber oils	...	...	22	+8 to +36	40	65
Whale			20	1·4762	22	+42 to +48	25	65-68
Turtle			30 50	1·4677 1·4665				
Dugong			...	...	...	...	25 40	60·3 52
Dolphin, body			15	1·4708	...	..	15	67·7
Porpoise, body			...	...	...	...	25 40	54·8 46·3
Brown fish			...	...	...	...	25	62·7
Chrysalis	Terrestrial animal oils		20	1·4757				
Egg			25	1·4713	...	...	25	68·5
Sheep's foot			...	...	22	0		
Horses' foot			...	...	...	− 6 to − 12		
Neat's foot			20	1·4681	22	− 1 to − 3	20	64·2
Parkia	Vegetable fats		...	...	...	...	25 40	67·2 58·8
Pongam			...	...	...	...	40	70-78
Laurel			40	1·4643	...	...	25 40	80 72
Margosa			...	...	...	...	40	52
Inukusu			25	1·4646				
Mowrah seed			...	...	...	...	40	52·1
Njave			...	...	...	...	40	52
Palm			60	1·4510				
Nutmeg butter		Myristica group	40	1·4704	...	...	40	61-67
Phulwara butter			...	...	...	...		48·2
Cacao butter			60	1·4496	...	...	40	46-47·8
Chinese vegetable tallow			...	...	...	− 23	40 50	38
Kokum butter			25	1·4628				
Palm nut		Cocoa nut oil group	60	1·4431	...	...	40	36·5
Cocoa nut			60	1·4410	...	...	40	34
Tonka butter			...	...	...	...	...	47
Myrtle wax			80	1·4363				

Oil, Fat, or Wax.	Class.	Group.	Refractive Index.					
			n_D		Oleo-refractometer.		Butyro-refractometer.	
			°C.		°C.	Degrees.	°C.	Degrees.
Lynx	Animal fats	Semi-drying fats	...	...	...	...	20	70
Wild duck			...	...	...	...	45	55·5
Marmot			...	...	...	...	40	59·4
Horse			...	...	...	...	40	53·7
Hare			...	...	...	...	40	49
Rabbit (tame)		Non-drying fats	...	...	...	...	40	49
Goose (domestic)			...	...	...	...	40	50-50·5
Human (adult)			...	...	...	...	40	49·6-53·1
Lard			60	1·4539	22	-12·5	40	45-57
Beef marrow			...	...	...	...	25	55·3
Beef tallow			60	1·4510	...	...	40	49
Mutton tallow			60	1·4501				
Butter			60	1·448-1·445	45	-25 to -31	40	41-42
Stag			...	...	...	...	40	44·5
Sperm oil	Liquid waxes		20	1·4650	22	-12 to -17·5	40	46·2
Arctic sperm oil			...	...	22	-13		
Carnaüba wax	Solid waxes	Vegetable waxes	...	...	...	...	40	65·7-69
Wool wax		Animal waxes	40	1·4781 -1·4822				
Beeswax					...	...	62	29·5-30
			75	1·4398 to 1·4451			40	42·9-45·6

The influence of food on the refractometer number of animal fats has been studied by *Polenske*;[1] he found that considerable quantities of cotton cake are required to produce (by feeding) an increase of the butyro-refractometer number in the case of hogs. Since the different foods considerably influence the proportion of unsaturated glycerides in animal fats (see Vol. II. Chap. XIV. "Animal Fats") and the refraction of unsaturated acids is notably higher than that of saturated acids, the influence of food naturally shows itself in the rise of the refraction (see Vol. II. Chap. XIV. "Butter Fat").

The changes which are produced in the refractive indices by the heating of oils and fats have been studied by *Utz*. His results are reproduced in the following table:—

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[1] *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1906, 567.

[TABLE

	Original Oil or Fat.		Heated One Hour in Water Oven.		Heated Three Hours in Water Oven.		Heated Ten Hours in Water Oven.		Heated Two Hours at 145° C.	
	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.	Refractive Index.	Butyro-refractometer.
Refraction at 20° C.										
Cotton seed oil .	1·4780	79·4	1·4780	79·4	1·4799	82·7	1·4813	85·2	1·4825	87·3
Cod liver oil .	1·4778	79·1	1·4776	78·7	1·4804	83·6	1·4805	83·8	1·4823	86·9
Olive oil . .	1·4688	64·5	1·4689	64·7	1·4696	65·7	1·4696	65·7	1·4698	66·1
Sesamé oil .	1·4730	71·1	1·4730	71·1	1·4731	71·3	1·4732	71·4	1·4738	72·4
Refraction at 40° C.										
Butter fat (fresh)	1·4536	41·7	1·4535	41·5	1·4538	42·0	1·4539	42·1	1·4548	43·4
,, (old) .	1·4533	41·3	1·4534	41·4	1·4540	42·3	1·4549	43·6	1·4554	44·3
Cacao butter .	1·4537	41·8	1·4535	41·5	1·4570	46·6	1·4574	47·2	1·4583	48·5
Cocoa nut oil .	1·4497	36·3	1·4498	36·4	1·4493	35·7	1·4500	36·7	1·4505	37·4
Lard . . .	1·4606	51·9	1·4606	51·9	1·4605	51·7	1·4617	53·6	1·4625	54·8
Tallow (Beef) .	1·4551	43·9	1·4550	43·7	1·4570	46·6	1·4580	48·0	1·4586	48·9
,, (Mutton)	1·4550	43·7	1·4550	43·7	1·4568	46·3	1·4582	48·3	1·4588	49·2

For the changes in the refraction which oils undergo on blowing, see Chap. VIII. and Vol. III. Chap. XV. " Blown Oils."

Procter[1] proposed to calculate the specific refraction of oils and fats. Little practical importance attaches, however, to this constant; hence the reader must be referred to the original paper.[2]

4. Rotatory Power of the Plane of Polarisation

The earliest observations made by *Bishop*[3] in a *Laurent's* saccharimeter with a 200 mm. tube are reproduced in the following table :—

Kind of Oil.	Rotation in Saccharimeter. Degrees.
Almond oil, sweet	−0·7
Arachis oil	−0·4
Colza oil (French)[4]	−2·1
,, (Japanese)	−1·6
Linseed oil	−0·3
Walnut oil	−0·3
Poppy seed oil	0·0
Olive oil	+0·6
Sesamé oil, cold expressed	+3·1
,, ,, warm expressed	+7·2
,, ,, 1878	+4·6
,, ,, 1882	+3·9
,, ,, 1882	+9·0
,, ,, Indian	+7·7

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[1] *Journ. Soc. Chem. Ind.*, 1898, 1023; cp. Lewkowitsch, *ibid.*, 1898, 1025.

[2] Cp. also J. Klimont, *Zeits. f. angew. Chem.*, 1911, 254.

[3] *Journ. Soc. Chem. Ind.*, 1887, 750.

[4] Cp. Vol. II. Chap. XIV. "Rape Oil."

Peter,[1] who also used *Laurent's* saccharimeter, found that almond, rape, hemp seed, linseed, and poppy seed oils are lævo-rotatory, whilst some specimens of arachis oil were dextro-rotatory, others again lævo-rotatory. *Thoerner*[2] examined almond, rape, linseed, arachis, and poppy seed oils in a 200 mm. tube in *Wild's* polaristrobometer, but leaves it open to doubt whether definite rotations occur. For castor and sesamé oils the numbers + 6·4° and + 1·0° respectively were ascertained.[3]

The foregoing observations seemed to point to the conclusion that, with the exception of castor oil (the rotatory power of which is satisfactorily accounted for by the asymmetric carbon-atom in ricinoleic acid), the optical activity was not caused by the glycerides themselves, but was due to small proportions of optically active substances, such as sitosterol (phytosterol) in the case of a lævo-rotatory oil. In the case of sesamé oil, the dextro-rotation must be due to the presence of sesamin. With regard to " Nux Vomica Fat " see Vol. II. Chap. XIV. For an optically active dextro-rotatory substance in cottonseed oil see Vol. II. Chap. XIV. " Cottonseed Oil."

In fish oils, liver oils, and blubber oils, slight rotations of the plane of polarisation to the left were observed (see Vol. II. Chap. XIV.). (Exceptionally, dextro-rotation has been recorded for porpoise body oil.) In these cases the optical rotation is attributable to small proportions of cholesterol contained in these oils. *Lindner*[4] has shown that in the case of some fish, liver, and blubber oil the magnitude of optical rotation stands in direct proportion to the amount of cholesterol in the oils. The strong optical rotation of wool wax can only be due to the large proportion of cholesterol and isocholesterol it contains.

The opinion which was therefore widely held that oils and fats themselves do not rotate the plane of polarisation, and hence that the determination of the optical rotation afforded little information of a discriminative nature, has been invalidated by the observations recorded in the following table :—

Oil.		Optical Rotation.	
Stillingia		− 6° 45′	in 200 mm. tube.
Chaulmoogra	$[\alpha]_D^{15}$	+ 52°	,,
Hydnocarpus, expressed		+ 57·7°	,,
,, extracted		+ 56·2°	,,
Lukrabo, expressed		+ 42·5°	,,
,, extracted		+ 51°	,,

The optical rotations recorded in this table are not caused by non-glyceridic substances, but are due to the configuration of the fatty acids themselves. In the case of chaulmoogra oil, *Lewkowitsch*[5] has shown that the optical rotation is even retained by the hydrocarbons which are formed on distilling this oil destructively.

[1] *Bull. Soc. Chim.*, 1887, 483.

[2] *Journ. Soc. Chem. Ind.*, 1895, 43.

[3] Cp. also Rakusin, *Chem. Centr.*, 1905, ii. 523 ; Lythgoe, *Journ. Amer. Chem. Soc.*, 1905, 887 ; Rakusin, *Chem. Zeit.*, 1906, 143.

[4] *Inaug. Dissert.*, Halle a. S., 1909.

[5] *Berichte*, 1907, 4161.

Since very few exotic oils and fats have been examined with regard to optical activity, it is not unlikely that a larger number of optically active fats may occur in nature than have been observed hitherto.

Thus, a short time ago, the great importance which optical rotation has for the identifications of fats became apparent, when a new fat appeared in the market under the name of "Marotti oil" ("Cardamom fat") which had been used in the manufacture of margarine and produced toxic effects. The optical rotation observed on a specimen of this oil enabled the author to assign to it at once its place in the system of oils and fats, as one of the fats belonging to the "Chaulmoogra oil group" (Vol. II. Chap. XIV.). It may be added that the presence of the fat, even in small proportions in the margarine, could be readily detected by means of the polarimeter.

It is therefore desirable not to omit the examination of new oils and fats for optical activity.

From the point of view of their optical activity, oils and fats may be subdivided into two classes.

(1) Oils and fats the optical activity of which is due to the presence of foreign active substances, such as sitosterol (phytosterol), cholesterol, sesamin, resins, methylheptylcarbinol, methylnonylcarbinol, etc.

(2) Oils and fats the optical activity of which is due to the configuration of the fatty acids themselves, as in the case of castor oil and, especially, the oils belonging to the chaulmoogra group.

It has been shown above (Chap. I. p. 18) that the naturally occurring triglycerides (as also α-monoglycerides and "mixed diglycerides," p. 11) may represent racemic compounds.[1]

With regard to the optical rotation of waxes cp. Vol. II. Chap. XIV. under "Carnaüba Wax," "Beeswax," and "Rump Gland Wax."

It may also be pointed out that the optical examination in a polarimeter may assist in detecting optically active foreign substances. Thus in case a linseed oil be found to be strongly dextro-rotatory, the presence of rosin oil may be suspected.

5. Microscopic Appearance

Although the microscope has been frequently recommended for the examination of fats and oils as to their purity and the detection of adulterants, microscopical examination has until recently been of limited use only. It was chiefly employed in the detection of beef fat in lard. Latterly it has also been proposed for the detection of cocoanut oil in butter fat (*Cesàro*,[1] *Hinks*[2]). Some Belgian chemists, following *Cesàro*, seem to lay excessive stress on microscopic indications in the case of butter fat suspected of being adulterated with cocoa-nut oil. As this subject will be treated fully in Volume II. of this work, the reader is referred to the sections " Lard " and " Butter Fat."

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[1] The statement made by Neuberg and Rosenfeld, that they resolved monohexabromoolein by means of a lipase into an optically active hexabromo-olein and an active dibromostearic acid, has been shown by Lewkowitsch (*Chem. Zeit.*, 1908, 54; *Jahrbuch d. Chemie*, 1907, xvii. 409) to be erroneous.

Microscopic examination is of great assistance in the investigation of the unsaponifiable matter. Thus pure, well-crystallised cholesterol and sitosterol (phytosterol) can be easily distinguished from each other under the microscope (see Chap. IX.).

The application of the polarisation microscope to the examination of oils and fats was, up till now, more restricted still in practice, and appears to be limited to butter fat.

The examination of butter fat under the polarisation microscope was first carried out by *J. Brown* (in 1874) for the detection of margarine in butter. The principle of the method (described below as the *Brown-Taylor-Richards method*; cp. Vol. II. Chap. XIV. " Butter Fat ") is based on the property of all optically isotropic substances (*i.e.* those which crystallise in the regular system, or which are amorphous) of being optically inactive under the polarisation microscope, whilst optically anisotropic crystals, a class to which appear to belong glycerides crystallising from the melted state, show different colours[3] under the polarisation microscope, in consequence of double refraction.

6. Spectroscopic Examination

With the exception of palm oil, the more important oils and fats are whitish or yellowish; it is therefore impossible to detect any characteristic differences with the naked eye. On examining, however, the fats spectroscopically, characteristic absorption spectra are observed. Although these are not due to the fatty substance itself, but to the presence of minute quantities of colouring matters, they may serve in some instances to distinguish different oils. Thus an admixture of vegetable oils with those of animal origin may be detected by the characteristic absorption bands which chlorophyll produces. Olive oil and linseed oil give three absorption bands—a very dark one in red, a faint one in orange, and a distinct one in green. Sesamé oil produces a weak band in red, whilst castor oil gives no bands at all.[4]

Chautard subdivided the fatty oils into two classes, active and inactive oils, according to whether they absorb certain prismatic colours, or allow them to pass through unabsorbed.

Doumer groups the oils, according to their spectroscopical behaviour, into four classes :—

1. Oils showing the spectrum of chlorophyll: olive oil, hemp seed oil, and walnut oil.

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[1] *Bull. Acad. roy. Belgique*, 1907, 1004.

[2] *Analyst*, 1907, 160.

[3] Cp. also Wauters, *Bull. Soc. Chim. Belg.*, 1905 (19), 6.

[4] Vogel, *Praktische Spectralanalyse*, 1877, 279. H. Krüss and P. Krüss, *Kolorimetrie und quantitative Spektralanalyse im ihrer Anwendung in der Chemie*; L. Voss, 1909, Hamburg.

2. Oils without any light-absorbing power: castor oil and almond oil.
3. Oils absorbing the "chemical rays" of the spectrum whilst the red, orange, yellow, and part of the green rays remain unabsorbed. On examining such oils, the spectrum from red to green appears, therefore, quite normal, whilst the other portions of the spectrum are invisible. To this class belong rape oil, linseed oil, and mustard seed oil.
4. Oils showing absorption bands in the different parts of the spectrum: sesamé oil, arachis oil, and cotton seed oil.[1]

Zune, who resumed the study of the spectroscopic behaviour of oils, adopts *Chautard's* classification.[2]

Lifschütz[3] proposed a spectroscopic test for the detection of the smallest quantities of oleic acid, for which, however, there is no need in technical analysis.

Unna and Golodetz[4] examined the absorption spectra given by cholesterol and isocholesterol; they are of the opinion that it is possible, by a spectroscopic method, to recognise both cholesterol and isocholesterol in a solution of acetic anhydride. It is essential that free fatty acids be entirely absent, as they interfere very seriously with the absorption spectra of the cholesterols.

Marcille,[5] who recently studied the absorption spectra of oils, arrives at the conclusion that vegetable oils do not show any essential difference as regards absorption spectra, as the only substance which produces the spectrum is chlorophyll. Since olive oil contains a much larger amount of chlorophyll than seed oils, olive oil can be easily recognised. Hence *Marcille* proposes the spectroscopic method for the recognition of olive oil in preserved sardines. He is also of the opinion that the spectroscopic method would allow to distinguish between olive pulp oils ("huiles de ressence") and the quality of oil represented by "huiles de grignon" (see "Olive Oil," Vol. II.).

7. Colorimetry

The measurement of the depth of colour does not play as yet the same important part in the examination of oils and fats which it does in the case of mineral burning oils. The commercial valuation as regards colour is therefore mostly based on inspection with the naked eye. In the United States, however, greater importance is attached to the scientific measurement of depth of colour. Thus "prime summer yellow" cotton seed oil is graded on the basis of indications furnished by *Lovibond's* tintometer (see Vol. II. Chap. XIV. "Cotton Seed Oil"). If colorimetric measurements should acquire greater importance, *Lovibond's* tintometer is the instrument most likely to be adopted generally; other colorimeters such as *Stammer's*, *Laurent's*, *Gosse's*,

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[1] Cp. Kenrick, *Analyst*, 1895, 136.

[2] *Analyse des Beurres*, ii. 48.

[3] *Zeits. f. phys. Chem.*, 1908 (56), 446.

[4] *Biochem. Zeits.*, 1909, 484.

[5] *Ann. des Falsif.*, 1910 (3), 423.

Wolf's, *Heele-Gallenkamp's*, and *Wilson's* chromometer are used in the examination of mineral oils, but have not been applied yet generally to the examination of oils and fats.[1] It may be added that *Barbet* proposed as a standard the colour shown by a one per mille iodine solution in a thickness of 1 cm.

8. Viscosity

Viscosity may be defined as the resistance the smallest particles offer to their sliding past one another, in other words, the viscosity of an oil is its internal friction. This internal friction by no means bears any known relation to the density of a liquid. A useful determination of the viscosity is based on *Poiseuille's* law[2] of the flow of a liquid through a capillary tube. This law is expressed by the following formula :—

$$\mu_1 = \frac{\pi p r^4}{8vl} \cdot t$$

where μ_1 is the coefficient of the internal friction or viscosity ;
p the pressure on the unit surface of the orifice of the capillary tube ;
r the radius of the tube ;
l the length of the tube ;
v the volume of liquid that has passed through the apparatus in t seconds.

This law holds good only if $l = 2r$.

For practical purposes it would be too tedious to use apparatus having capillary efflux tubes ; hence, for the commercial examination of oils, the diameter of the efflux tube is usually taken somewhat large, and the height of the column of the liquid somewhat small.

The viscosity is usually determined by ascertaining the times two equal volumes of the liquids under comparison take to flow through a narrow aperture under exactly the same conditions. It should be noted that the numbers so obtained are entirely arbitrary, giving no information as to the internal friction of the oils. Different apparatus —" viscosimeters "—give entirely differing numbers. Nevertheless, such numbers can be employed usefully for the identification of different oils.

For a rough comparison, it may suffice to use a wide glass tube drawn out, at the lower end, to a narrow aperture about 2 mm. in diameter and having upper and lower marks for the exact measurement of the volume of liquid.

In the earliest experiments, carried out by *Schübler*, a glass tube of

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[1] Cp. also Procter, *Journ. Soc. Chem. Ind.*, 1910, 665 ; Autenrieth and Königsberger, *Zeits. f. ang. Chem.*, 1912, 1169.

[2] With regard to the determination of the absolute viscosity cp. Vol. III. Chap. XV. "Lubricating Oils—Lubricants." Apparatus for the determination of the internal friction have been constructed by Poiseuille, Petroff, Traube, and Guchmann.

2 cm. diameter and 10 cm. height, having attached to it a narrow tube of 1·6 mm. diameter, was employed. The results are reproduced in the following table :—

Name of Oil.	Number of Seconds required at		Viscosity at	
	+15° R.	+7·5° R.	+15° R.	+7·5° R.
Castor oil	1830	3390	203·3	377·0
Olive oil	195	284	21·6	31·5
Colza oil	162	222	18·0	22·4
Winter rape oil	159	204	17·6	22·6
Beechnut oil	158	237	17·5	26·3
White mustard oil	157	216	17·4	24·0
Almond oil	150	209	16·6	23·3
Summer rape oil	148	205	16·4	22·7
Rape oil	142	200	15·8	22·2
Mustard seed oil	141	175	15·6	19·4
Summer rubsen oil	136	198	15·1	22·0
Poppy seed oil	123	165	13·6	18·3
Cameline oil	119	160	13·2	17·7
Sunflower oil	114	148	12·6	16·4
Peach kernel oil	93	132	10·3	14·7
Walnut oil	88	106	9·7	11·8
Linseed oil	88	104	9·7	11·5
Hemp seed oil	87	107	9·6	11·9
Distilled water	9	9	1·0	1·0

On dividing the number of seconds required for an oil by that required for water at the same temperature, a number was obtained which was termed *specific viscosity*, or in short, *viscosity*. Thus the viscosity of castor oil, according to *Schübler*, was $\frac{1830}{9} = 203{\cdot}3$ at 15° C.

In practice, the viscosity of oils is frequently compared with that of rape oil. *Redwood*[1] found, from a number of tests carried out with refined rape oil in his viscosimeter, that 535 seconds may be considered as the average number required for the outflow of 50 c.c. of refined rape oil at 60° F. (15·5° C.).

Taking rape oil as a standard, and putting its viscosity = 100, the viscosity of any other oil under examination would then be found by multiplying the number of seconds required by the outflow of 50 c.c. by 100, and dividing by 535. In case the sample has a specific gravity differing from that of rape oil—0·915 at 60° F.—*Redwood* introduces a correction by multiplying the result by the specific gravity of the sample, and dividing by 915. If n be the number of seconds for an oil under examination, and s its specific gravity, the following formula is arrived at :—

$$\text{Viscosity} = \frac{n \times 100 \times s}{535 \times 915} = \frac{n \times 100 \times s}{489525}.$$

Since, however, there is no correlation between specific gravity and viscosity (see above), I consider it more useful to record the numbers as obtained by direct determination of the viscosity.

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[1] *Journ. Soc. Chem. Ind.*, 1886, 127.

Engler uses water as the standard liquid; 200 c.c. of water at 20° C. require 53 seconds to flow through his apparatus. If n be the number of seconds required by an oil under the same conditions, the quotient $\frac{n}{53}$ represents the "specific viscosity" of the oil in *Engler's* apparatus.

In order to obtain comparable results, complete uniformity of construction in apparatus is essential. Passing over a number of forms of apparatus that have been proposed from time to time,[1] I shall describe only three—those of *Redwood*, of *Saybolt*, and of *Engler*. The first apparatus has been adopted in this country by the War Department, the principal Railway Companies, and the Scottish Mineral Oil Association; the second is used privately,[2] but not officially, in the United States; [3] and the third occupies, in Germany, a position similar to that of *Redwood's* in this country. *Barbey's* "Ixomètre" is used in France. A description and illustration of this instrument will be found in the French edition of this work.[4] In Russia the *Lamansky-Nobel* apparatus is in general use.[5]

Redwood's viscosimeter [6] (Fig. 29) consists of a silvered copper oil-cylinder C, about $1\frac{7}{8}$ in. in diameter, by about $3\frac{1}{2}$ in. in depth. The bottom of this cylinder is provided with an agate jet D, the cup-shaped cavity of which can be closed by means of the plug E, formed of a small silvered brass sphere attached to a wire. Inside the oil cup and at a short distance from the top there is fixed a small bracket F, terminating in a point. This serves as a gauge of the height to which the oil must be filled. A thermometer T is immersed in the oil and supported by means of a clip holding the plug E. The cylinder C is surrounded with a copper jacket J, having a closed side tube K, by means of which the liquid in the jacket can be brought to any desired temperature. The heated liquid rising from K is uniformly distributed through the bath by means of a revolving agitator worked by the handle H. The temperature of the liquid is controlled by the thermometer T′. The whole instrument is supported on a tripod stand provided with levelling screws. Fig. 30 represents a plan of Fig. 29.

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[1] Dollfus, *Dingl. Polyt. Journ.* 153, 231; Vogel, *ibid.* 168, 267; Fischer, *ibid.* 236, 487. Lepenau, *Zeits. f. analyt. Chem.* 24, 465; Napier, *ibid.*, 1896, 361. See also Redwood, *Journ. Soc. Chem. Ind.*, 1886, 121; Mills, *ibid.*, 1886, 148; Hurst, *ibid.*, 1892, 418; Neumann-Wender, *ibid.*, 1895, 596; Killing, *ibid.*; Redwood, *Petroleum*, 1896, vol. ii. pp. 602-620. Meggitt, *Journ. Soc. Chem. Ind.*, 1902, 106. For Coleman-Archbutt's viscosimeter see Archbutt and Deeley, *Lubrication and Lubricants*, p. 140; cp. also Hackel, *Mitt. d. K. K. Technol. Gewerbe-Museum*, Vienna, 1905, xv. 36, 44; Courtois' United States patent 788,251. Chenevier, *Mém. de la Soc. des Sciences phys. et nat.*, Bordeaux, 1887, iii. 405. Schulz-Kolin, *Chem. Zeit.*, 1908, 891; French patent 388,671 (W. H. Houston); K. Arndt, *Zeit. f. Chem. Apparatenkunde*, 1908, 473, 500, 521, 549. W. Graff & Co., and H. Mikorey, German patent 207,177 and 207,178; Add. patent to patent 205,235; *Chem. Zeit. Rep.*, 1909, 178; *A. Baldus*, English patent 22,961, 1910; I. Kurzmann, a new Multi-viscosimeter, *Chem. Zeit.*, 1913, 234.

[2] See footnote 4, p. 352.

[3] Some Railway Companies in the United States use Doolittle's Torsion Viscosimeter.

[4] Lewkowitsch, *Technologie et analyse chimiques des huiles, graisses et cires, traduit par E. Bontoux*, Paris, 1906, p. 276. A table containing a number of observations will be found *ibid.* p. 283.

[5] Lamansky, *Dingl. Polyt. Journ.* 248, 29. Lamansky's viscosimeter has been improved in the Nobel refineries at Baku, cp. *Chem. Rev. über Fett. u. Harz-Industrie*, 1897, 90.

[6] *Journ. Soc. Chem. Ind.*, 1886, 126.

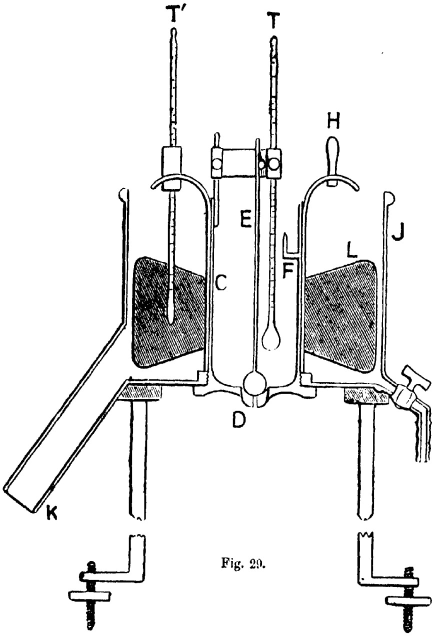

Fig. 29.

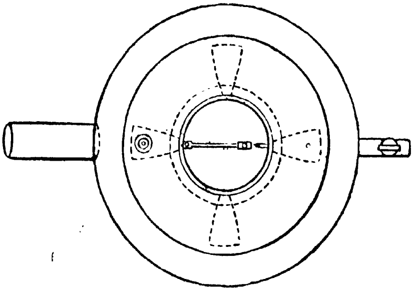

Fig. 30.

The viscosimetric observation is made in the following manner:— The copper jacket is filled with water, for temperatures up to about 95° C., and for higher temperatures with a suitable mineral oil, to a height corresponding with the pointer F in the cylinder C. After the liquid in the bath has been heated to the required temperature, the sample of oil, purified and dried, and previously brought to the same temperature, is poured into C, until its level just coincides with the point of the gauge. Great care must be taken that this level be reached exactly, and that the temperature remain constant during the observation. A narrow-necked flask, holding 50 c.c. to a point marked on the neck, is then placed beneath the jet in a vessel containing a liquid of the same temperature as the oil. The plug is then raised, and the number of seconds required for 50 c.c. of the oil to flow out is carefully observed by means of a chronometer. At least two tests should be made at the same temperature; if due care has been exercised, the two observations will be found closely concordant.

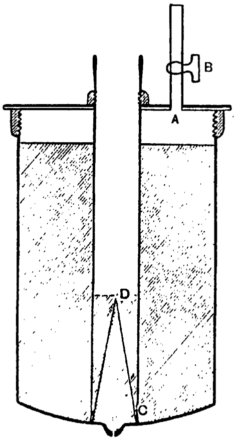

Fig. 31.

Allen [1] modified *Redwood's* viscosimeter with a view to maintaining a given head of oil throughout the experiment.[2] For this purpose the top of the oil-cylinder (Fig. 31) is fitted with an air-tight cap perforated by two holes, one of which is furnished with a tap B, whilst into the other a tube is screwed air-tight. This tube C is prolonged on two sides till it is in contact with the agate orifice, whilst the angles of the inverted V-shaped slits, cut on each side, terminate at a definite height, D, above the orifice. The cylinder is completely filled with oil before commencing an experiment, the tap B is closed, and the orifice opened till the oil sinks in the inner tube to the level D. Air then bubbles in regularly at D, and rises into the closed space above the oil; when this is observed to happen, the oil is collected in a graduated cylinder. When using this apparatus, there is no necessity to collect exactly 50 c.c., because the oil runs through at a constant rate.

The same principle has been adopted by *E. Schmid* [3] in the improved *Reischauer* viscosimeter (see Fig. 32).

These modified viscosimeters have, however, not been recognised officially.

Saybolt's viscosimeter.[4] The oil vessel of this apparatus is placed in a water-bath of considerable capacity. The jet of the viscosimeter is of metal, and is enclosed in a tube extending below the orifice. The oil vessel is contracted, as shown (Fig. 33), above the jet, and is cut away longitudinally on each side, to expose a glass tube which lines it.

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[1] *Journ. Soc. Chem. Ind.*, 1886, 131.

[2] For another "Constant Pressure Viscometer" cp. W. H. Patterson, *Proceed. Chem. Soc.*, 1913, 172.

[3] *Chem. Zeit.*, 1885, 1514.

[4] The description of this viscosimeter is taken from Redwood, *Petroleum*, vol. ii. p. 608. Saybolt's viscosimeter is not obtainable in commerce; it seems to be used exclusively, and privately, by the chemists of the Standard Oil Company. It is stated (*Chemical Engineer*, 1906, January) that three forms of the Saybolt viscosimeter, *A*, *B*, and *C*, are used. *A* serves for the examination of lubricating oils for dynamos and light machinery at 70° F.; *B* for the examination of dark, heavier, and more viscous oils at 70° F.; *C* for the determination of the viscosity of cylinder oil at 200° F. Tagliabue's viscosimeter is an improvement of the Saybolt viscosimeter in so far that only one instrument is required for the examination of all kinds of oil.

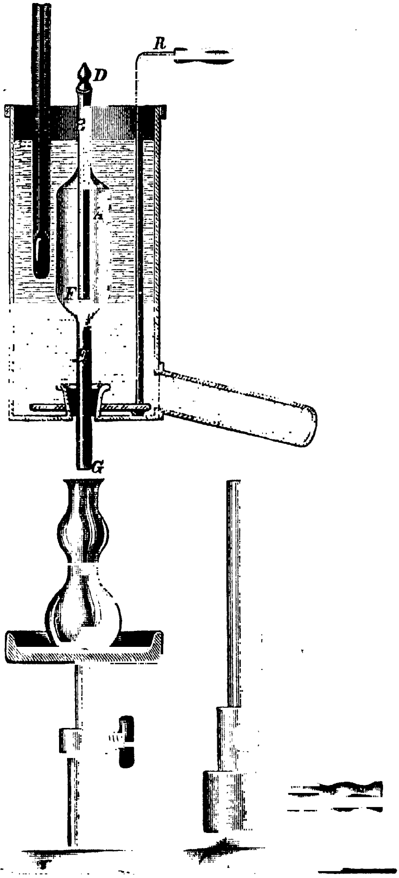

Fig. 32.

Glass windows are provided in the water-bath. The upper edge of the oil vessel is fitted with an oil-tight gallery having a raised edge, and communicating by a number of small holes with the oil vessel, which extends to the same level as the top of the gallery. For use, the water-bath is filled with water at the required temperature, a cork inserted in the mouth of the tube enclosing the jet, and the vessel filled with the sample of oil, until it overflows through the holes into the gallery. The oil is then stirred with a thermometer, and the temperature adjusted if necessary. On withdrawing the thermometer, the oil which it had displaced flows back from the gallery; the latter is then completely emptied by means of a pipette. The length of the oil column is, of course, determined by the position of the holes connecting the oil vessel with the gallery. The flow of oil from the jet is started by withdrawing the cork, and a stop-watch is set in motion. The watch is stopped when the operator sees the surface of the oil through the glass tube above mentioned.

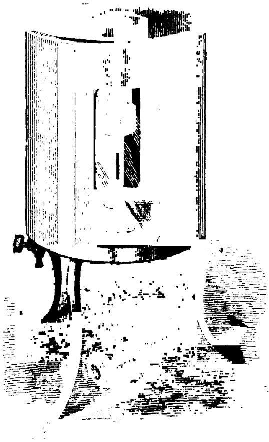

Fig. 33.

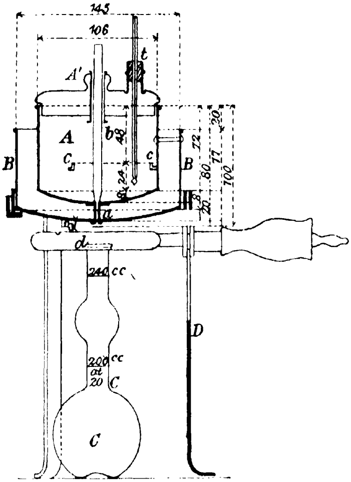

Fig. 34.

Engler's viscosimeter[1] in its latest form, as designed by him in conjunction with the officials of the Charlottenburg Mechanisch-Technische Versuchsanstalt, is shown in Fig. 34. The oil vessel, A, is, as a rule, made of sheet brass; for accurate determinations it is prescribed to use a viscometer, the inner surface of which is gold-plated. The vessel is closed by a cover, A′, perforated by two holes, into one of which the thermometer *t* is fitted, whilst the other serves to receive the plug *b*. The delivery tube *a* projecting from the convex bottom of the vessel A must be exactly 20 mm. long, and 2·9 mm. in diameter at the top and 2·8 mm. at the bottom.[2] The delivery tube is preferably made of platinum, as in course of time brass is attacked even by neutral oils. The plug *b* is made of hard wood. Three pointers *c* serve the double purpose of indicating the correct level of the apparatus and of marking the exact volume of 240 c.c. The vessel A is jacketed, vessel B serving as a receiver for mineral oil, which may be heated up to 150° C. by means of gas supplied through tube *d*. As shown in the figure, this jacket also surrounds the delivery tube *a*, thus preventing loss of heat whilst the oil flows out. The instrument is fastened on to the tripod D. Flask C bearing two marks on the neck for 200 c.c. and 240 c.c. respectively is placed under the efflux tube.

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[1] *Journ. Soc. Chem. Ind.*, 1893, 292.

[2] With regard to the influence of small deviations from the dimensions given above cp. W. Meissner, *Chem. Rev.*, 1910, 202.

Engler lays the greatest possible stress on the necessity of strictly adhering to the measurements given in Fig. 34.[1]

Recently *Engler's* viscosimeter has been somewhat modified by the introduction of a stirring apparatus.[2]

In order to test the instrument, the time taken by the outflow of 200 c.c. of water at the temperature of 20° C. is first determined. Vessel A is cleared with ether or petroleum ether and rinsed out with alcohol and water. Tube *a* is wiped out by means of a feather or filtering paper, and closed with the plug *b*. With the aid of the flask C, 240 c.c. of water are measured off and poured into vessel A. This should then be adjusted exactly up to the level of the pointers *c*. The mineral oil in B is warmed to 20° C. The water in A must have the same temperature. The dry flask C is placed under the delivery tube *a*, and when the temperature has remained constant, the plug is drawn and the time carefully noted (by means of a chronometer) which is required to fill the flask C up to the 200 c.c. mark. It is most important that the water in A should be completely at rest before the plug is drawn. The time required should be from 51 to 53 seconds for a correct instrument; repeated observations should not differ by more than 0·5 of a second.

Before an oil is examined, every trace of dirt and moisture must be removed from A by wiping out carefully and rinsing successively with alcohol and ether (or petroleum ether); finally the apparatus should be rinsed out with the filtered and dried oil. The oil is then poured into A, up to the pointers *c*, and heated to the desired temperature, at which it must be kept for at least two or three minutes before it is allowed to run out.

The following table gives a comparison of results based on a number of experiments with the three viscosimeters:[3]—

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[1] "The normal apparatus" is manufactured under the joint control of the Charlottenburg Technische Anstalt and the Karlsruhe Chemisch-Technische Versuchsanstalt, and may be also had from C. Desaga of Heidelberg. According to Engler's statements, apparatus from other sources are not made with the requisite care, and give discordant results; cp. W. Meissner, *Chem. Rev.*, 1910, 1202.

[2] Ubbelohde, *Chem. Zeit.*, 1907, No. 4; cp. also *ibid.* No. 3, and Ubbelohde, *Tabellen zum Englerschen Viskosimeter*, Leipzig, 1907.

[3] Redwood, *Petroleum*, vol. ii. p. 610.

Viscosimeter.	Seconds for outflow of	
	50 c.c. at 70° F.	200 c.c. at 20° C.
Redwood's . .	100	...
Saybolt's . .	56	...
Engler's . .	...	170

W. Meissner[1] gives the following table of comparison :—

	At °C.	Seconds for Outflow in Viscosimeters.			
		Engler's 200 c.c.	Engler's 200 c.c.	Redwood 50 c.c.	Saybolt-"Universal" 60 c.c.
Water	20	51·26	51·39	26·47	28·55
Rape oil	50	236·1	237·0	142·5	169·1
Rape oil	20	735·1	736·6	424·5	515·6
Lubricating oil . .	150	362·3	362·9	221·1	258·6
Lubricating oil . .	120	2525	2527	1490	1759

It will be seen that *Engler's* viscosimeter requires much more time than either of the other two apparatus. The proposal has therefore been made to shorten the time by noting the number of seconds after 50 c.c. or 100 c.c. have run out, and multiplying the number of seconds by empirically found "constants."[2] Surely, it would be much simpler to use an apparatus based on the outflow of 50 c.c.

As a rule, the viscosity of a lubricating oil is determined at a temperature approximating to that at which the oil is actually used. Since *Engler's* viscosimeter has been found unsuitable for observations at elevated temperatures, *Engler and Künkler*[3] designed a "viscosimeter for examination of oils under constant temperature." This instrument is represented by Fig. 34. It is an octagonal jacketed air-bath made of sheet brass, 35 cm. high and 20 cm. wide. The feet *a* stand in the ring of a tripod, and the level of the air-bath can be adjusted so as to control the level of the liquid in the viscosimeter itself, which is contained in the upper portion of the bath. The flame of a Bunsen burner is made to impinge on the arched copper plate *b*, protected by a sheet of asbestos. Above this is placed the tripod *c* and the measuring vessel *e*, supported by *d*, and protected from direct radiation from *b* by the asbestos plate *f*. Above this is the dividing plate *g*, supporting the four oval tubes *i* and the viscosimeter *k*. Plate *g* is perforated by the large hole *h*, through which the oil flows into the measuring vessel. Circulation of hot air into the upper chamber takes place through *h*, as also through the four oval tubes *i*. Through the cover of the instrument pass the thermometers *u*, *s*, the axis of the stirring apparatus with the plug *t* for the delivery tube, and the jacketed funnel *v* for introducing the oil, previously heated to the required temperature in the can H, which is also provided with a stirring apparatus and a thermometer fixed in its hollow axis. Windows *l* and *m* are fixed in the cover and also in the side; so that the level of the oil in the viscosimeter and the flow of the oil into the measuring vessel *e* can be observed.

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[1] *Chem. Revue*, 1912, 33, 44; 1913, 123.

[2] Singer, *Chem. Rev. über die Fett- u. Harz-Industrie*, 1807, 93, shows that the "constants" 5 for 50 c.c., and 2·34 for 100 c.c., give results agreeing with those found when allowing 200 c.c. to run out; L. Edeleanu and S. Dulugea propose to run out 20 c.c. only, *Chem. Rev.*, 1910, 299; cp. also Offermann, *Chem. Rev.*, 1911, 272.

[3] *Journ. Soc. Chem. Ind.*, 1890, 654.

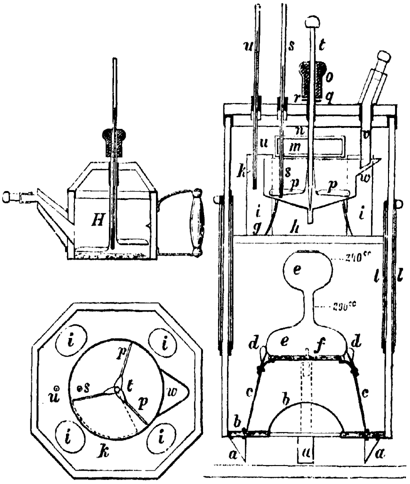

Fig. 35.

The method of using the instrument, and the manipulations required for making an observation, need no detailed description. The fact that the apparatus satisfies the required condition of constant temperature is proved by the following observation: If the empty viscosimeter be heated to 100° C., the temperature is equable and constant in all parts of the bath, with the exception of the lowest stratum of air in *k* itself, owing, no doubt, to the absence of circulation. This drawback, however, disappears with the introduction of the oil. At temperatures exceeding 100° C., the air above the oil vessel has a somewhat lower temperature, but the difference does not amount to more than 4° C. at 150° C.[1]

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[1] A similar principle is made use of in Marten's viscosimeter, *Mitt. Königl. Technisch. Versuchsanst.*, Berlin, 1889, Ergänzungsheft, v. 6.

A description of *Künkler's* viscosimeter for the examination of small quantities of lubricating oils will be given in Vol. III. Chap. XV.

Traube[1] condemns the viscosimeters described here on the ground that, theoretically, it is not permissible to compare the respective times of delivery of heavy and light oils, and still less the times of delivery of oils and water observed in one and the same apparatus. For a description of the apparatus by which *Traube* proposes to replace the viscosimeters at present in use, the reader must consult the original paper.

The viscosimetric examination of fatty oils does not furnish results of a discriminative nature, and the somewhat exaggerated details, the observance of which is recommended especially with the *Engler* viscosimeter, vastly overestimate the practical importance of the viscosimetric determination;[2] only sperm oil, a liquid wax, is very characteristic in this respect (cp. Vol. II. Chap. XIV.). For this reason sperm oil was used as the standard lubricant for all classes of light machinery before the use of mineral oils had become general.

The following tables give the viscosities of sperm oil, of some fatty oils, and of mineral oils largely used for lubricating purposes. It will of course be observed that the figures given by different observers vary. This is no doubt due to the difference of the specimens under examination.

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[1] *Journ. Soc. Chem. Ind.*, 1887, 414.

[2] Cp. W. Meissner, *Chem. Rev.*, 1910, 202.

[TABLE

Viscosity of some Fatty and Mineral Oils in Redwood's Viscosimeter

50 c.c. of water at 60° F. require 25·5 seconds.

°F.	Rape Oil, Refined.	Sperm Oil.	Neat's Foot Oil.	Beef Tallow.	American Mineral Oil.			Russian Mineral Oil.		
					Sp. gr. 0·885.	Sp. gr. 0·913.	Sp. gr. 0·923.	Sp. gr. 0·909.	Sp. gr. 0·915.	Sp. gr. 0·884.
50	712·5	...	...	...	145·0	425·0	1030·0	2040·0	2520·0	
60	540·0	177·0	470·0	...	105·0	295·5	680·0	1235·0	1980·0	
70	405·0	136·8	366·0	...	90·0	225·0	485·0	820·0	1320·0	
80	326·0	113·0	280·0	...	73·0	171·0	375·0	580·0	900·0	
90	260·0	96·0	219·25	...	63·5	136·0	262·0	426·0	640·0	
100	213·5	80·5	174·75	...	54·0	111·0	200·0	315·0	440·0	1015·0
110	169·0	70·5	147·4	...	50·0	89·5	153·0	226·0	335·0	739·5
120	147·0	60·5	126·0	...	47·0	78·0	126·0	174·0	245·0	531·0
130	123·5	57·0	112·0	...	44·75	63·5	101·0	135·5	185·0	398·5
140	105·5	50·75	88·4	...	41·0	58·0	82·0	116·0	145·0	317·5
150	95·5	49·0	75·5	...	37·5	52·0	70·5	95·0	115·0	250·0
160	85·0	47·5	70·0	...	...	46·0	63·5	83·5	93·5	200·0
170	76·0	46·0	62·0	...	...	...	58·0	70·5	77·5	161·0
180	69·0	44·5	56·5	...	...	...	52·5	61·5	67·5	134·5
190	64·5	43·0	53·0	...	...	...	47·0	56·5	61·0	115·5
200	58·5	42·0	50·4	54·75	...	...	42·0	48·5	54·0	99·25
210	54·0	40·75	48·5	...	...	...	40·0	...	...	85·0
220	50·0	39·0	47·0	...	...	...	38·0	...	...	77·0
230	47·25	36·75	45·8	...	...	...	...	...	...	70·5
240	45·5	35·75	44·6	...	...	...	...	...	...	64·5
250	43·25	34·75	44·0	40	...	...	...	...	...	59·25
260	...	33·75	43·5	...	...	...	...	...	...	54·0
270	...	32·75	43·0	...	...	...	...	...	...	48·5
280	...	31·85	41·5	...	...	...	...	...	...	46·5
290	...	30·75	41·0	...	...	...	...	...	...	44·25
300	...	30·0	38·0	...	..	...	...	...	...	42·4
310	...	...	35·0							
320	...	...	33·8							

[TABLE

	Specific Gravity at 60° F.	Viscosity (Redwood's Viscosimeter).			Flash Point. Close Test.	Cold Test.
		70° F.	120° F.	180° F.	°F.	°F.
Refined Mineral Oils—[1]		Standard for Viscosity. Sperm Oil at 70° F. = 100.				
Scotch	0·890-0·895	100-130	40-50	..	320-350	32
	0·885-0·890	75-100	35-40	..	300-325	32
	0·875-0·880	50-60	25-30	..	300-325	32
American	0·915-0·920	400-425	90-100	35-40	375-425	32
	0·905-0·910	200-225	55-65	..	350-400	32
	0·885-0·890	75-100	35-40	..	325-350	32
	0·875-0·880	65-75	30-35	..	325-350	32
Russian	0·910-0·915	1200-1500	200-250	50-70	400-425	25
	0·905-0·912	700-800	125-150	45-50	350-375	25
	0·895-0·900	220-250	60-65	..	325-350	15
	0·895-0·900	125-175	..	..	300-325	10
Natural (dark) Mineral Oils—		Standard for Viscosity. Tallow at 180° F. = 100.				
American summer, dark .	0·890-0·895	..	250-300	70-75	400-425	40-50
,, medium . .	0·880-0·885	550-700	110-125	40-50	350-400	25-30
,, winter . .	0·880-0·885	350-400	90-100	35-40	325-375	25-30
Russian residuum . .	0·910-0·915	750-1000	150-200	45-60	250-300	25-30
Natural, and Filtered Mineral Oils—						
American heavy dark .	0·900-0·905	..	1750-2000	350-400	500-550	40-45
,, extra dark .	0·900-0·905	..	2000-2500	400-450	525-575	35-40
,, medium dark .	0·895-0·900	..	1200-1400	300-350	500-525	40-45
,, heavy filtered .	0·890-0·895	..	1400-1500	300-350	500-550	60-70
,, medium filtered	0·890-0·895	..	1000-1200	250-300	500-525	65-70
,, light filtered .	0·885-0·890	..	885-1000	200-250	450-500	75-80
,, fluid filtered .	0·885-0·890	..	1200-1400	300-350	500-550	40-45
,, ,, ,,	0·885-0·890	..	900-1000	225-275	450-500	45-50
Southern sperm oil . .	0·8807	100·1	45·4	..	457·5*	41·7
Arctic sperm oil . . .	0·8804	105·3	47·2	..	446·2*	39·2
White whale oil . . .	0·9207	187·7	71·3	..	476·0*	27·2
Neat's foot oil . . .	0·9178	247	82·4	..	470·3*	34·4
Lard oil	0·9172	223·2	79·4	..	493·9*	39·6
Olive oil	0·9167	213·2	75·0	..	437·5*	27
Rape oil, East India, refined .	0·916	250·4	88·1	..	478·6*	26·4
,, Black Sea, refined .	0·9209	226·9	78·8	..	465·4*	27
Cotton seed oil, refined . .	0·9235	190·4	69·8	..	523 *	30
Castor oil	0·963	2500	390	..	487 *	0

[1] Cp. *Carpenter-Leask*, pp. 263-291.

* Mean Values.

Viscosities of some Oils and Fats (Crossley and Le Sueur)

Kind of Oil.	Number of Seconds in Redwood's Viscosimeter, 50 c.c. of water at 70° F. = 25·4 Seconds.	Kind of Oil or Fat.	Number of Seconds in Redwood's Viscosimeter, 50 c.c. of water at 70° F. = 25·4 Seconds.
Linseed . .	212	Garden cress .	322
Tung . . .	858-1433 (water 28 sec.)	Radish seed .	385
		Arachis . .	307-429
Walnut . .	232	Olive . . .	312
Safflower . .	249·1-294	Mahua . .	90-107
Poppy seed . .	254-259	Phulwara . .	110·4
Amoora . .	376	Malabar tallow .	101-104
Niger seed . .	263-293	Kokum butter .	101
Argemone . .	269-272	Cocoa nut . .	64

Kind of Oil or Fat.	Specific Gravity at 17·5° C.	Viscosity (Engler's Viscosimeter).			
		20° C.	50° C.	100° C.	150° C.
Rape oil, crude	0·920	9·03	4·0	1·78	1·34
Rape oil, refined	0·911	11·88	4·9	2·05	1·40
Olive oil	0·914	10·3	3·78	1·80	
Castor oil	0·963	...	16·46	3·01	
Linseed oil	0·930	6·36	3·2	1·76	
Tallow	0·951	...	5·19	2·50	1·73
Neat's foot oil	0·916	11·63	4·44	1·92	

Kind of Oil or Fat	Specific Gravity at 17·5° C.	Flash Point. °C.	Viscosity (Engler's Viscosimeter).	
			At 50° C.	At 100° C.
Russian cylinder oils	0·911-0·923	183-238	10·2-16·2	2·0-2·8
,, machine oils	0·893-0·920	138-197	5·8-6·3	1·5-1·8
,, spindle oils	0·893-0·895	163-167	3·1-3·4	1·4-1·5
American cylinder oils	0·886-0·899	280-283	...	4·1-4·8
,, machine oils	0·884-0·920	187-260	4·2	1·6
,, spindle oils	0·908-0·911	187-200	3·1-3·3	1·4-1·6
Rape oil, crude	0·920	265	4·0	1·7
,, ,, refined	0·911	305	4·9	2·0
Olive oil	0·914	305	3·7	1·8
Castor oil	0·963	275	16·4	3·0
Linseed oil	0·930	285	3·2	1·7
Tallow	0·951	265	5·2	2·5

A correlation between viscosity and iodine value is shown in the following table due to *Crossley and Le Sueur*:[1]—

Kind of Oil.	Iodine Value.	Viscosity (Redwood's Viscosimeter). Number of Seconds at 70° F.
Arachis	92·43	429·3
	98·42	347·0
	98·47	350·1
	100·82	306·9
Argemone	119·91	272·0
	122·53	268·9
Rape	94·10	464·6
	96·66	413·8
	96·75	402·0
	96·25	393·2
	101·82	379·3
	101·84	371·8

This correlation, however, is not shown by the numbers recorded in the preceding tables.

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[1] *Journ. Soc. Chem. Ind.*, 1898, 990.

The viscosity of a mixture cannot be calculated from the viscosities of the components; in other words, viscosity is not an additive property. *F. Schulz*[1] has calculated an empirical formula for *Engler's* viscosimeter, basing himself on three experiments made with oils of widely differing viscosities as measured in *Engler's* apparatus.

Such an empirical formula may prove useful in practice, if it be required to prepare for commercial purposes (tenders) a mixture of a predetermined viscosity. *H. C. Sherman*, *T. T. Gray*, and *H. A. Hammerschlag*[2] also find that the *Engler* viscosity numbers were always lower than calculation would indicate.

9. Consistence

It has been pointed out already that any attempt to base a classification of oils, fats, and waxes on their consistence must lead to failure. The consistence of a fat is implicitly given by its melting and solidifying points.

Hence methods employing consistence as a means of examination have very limited application, and at best can only be used to discriminate various specimens of one and the same kind of oil. But even in those cases the determination of the solidifying and melting points of the oils themselves, or of their fatty acids, leads to more decisive results.

The first attempts to employ the determination of the consistence for analytical purposes were made by *Serra Carpi* and by *Legler*; in both cases the method was proposed chiefly for the examination of olive oil.

Serra Carpi[3] places on olive oil, previously cooled to - 20° C. for three hours, a cylindrical iron rod 2 mm. in diameter and 1 cm. long, and conical at the bottom. Weights are then put on to the rod until it sinks completely into the fat. Thus, for pure olive oil 1700 grms. and for cotton seed oil 25 grms. were required.

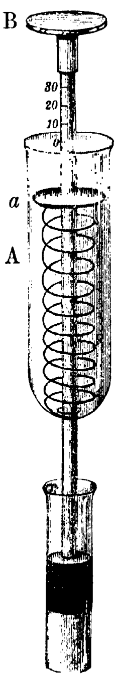

Fig. 36.

Whilst *Serra Carpi* examines the oil itself, *Legler* proposes to treat it first with nitrous acid so as to produce the harder elaïdin (see "Elaïdin Test," Chap. VII.). He recommends the apparatus[3] shown in Fig. 36, which consists of a strong glass tube A, wherein a stout glass rod is allowed to slide. The rod is widened at *a* into a disc holding down a spring, which easily responds to a weight of 20-50 grms. placed on the top B. The point to which the glass rod sinks by its own weight is marked on the rod by 0; from there upwards, marks indicating millimetres are scratched on the rod. The same principle and substantially the same apparatus have been recommended by *Brullé*[1] (for the examination of butter). *Sohn*[2] proposes three forms of apparatus, and lays down the following rules, strict adherence to which he enjoins:—

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[1] *Chem. Revue*, 1909, 297.

[2] *Journ. Soc. Chem. Ind.*, 1909, 13.

[3] *Zeits. f. analyt. Chem.* 23, 566.

(1) The rod must descend in an absolutely perpendicular direction.
(2) It must slide in its bearing with the least possible friction.
(3) Conditions of temperature must be constant.
(4) Vessels of one diameter must be used for the material under examination.
(5) The rod must enter the centre of the vessel, or at a fixed distance from the circumference.
(6) The same depth of material must always be used.
(7) The material must be allowed to rest a certain fixed time before testing.

With regard to testing the consistence of polymerised tung oil, cp. Vol. II. Chap. XIV. under "Tung Oil."

10. Solubility

Oils and fats dissolve readily in ether, carbon bisulphide, chloroform, carbon tetrachloride, benzene, petroleum, and petroleum ether. The differences as regards solubility, however, are not so pronounced that individual oils and fats can be thereby differentiated.

Hence, methods such as that recommended by *Horsley*[3] to differentiate butter fat from lard by the different solubility in organic solvents are either useless or of very limited applicability, and should only be resorted to in case all other methods fail. In *Bjorklund's* ether test (see Vol. II. Chap. XIV. "Cacao Butter"), or after a systematic fractionation of glycerides has been carried out with a view to obtaining pure glycerides (see Chap. XII.), differences in solubility furnish useful indications. In this connection it should be noted that diglycerides are much more insoluble in petroleum ether than are triglycerides.[4]

Castor oil differs from all other natural oils and fats by its comparative insolubility in petroleum ether and paraffin oil (see Vol. II. Chap. XV. "Castor Oil").

Castor oil further differs from all other oils and fats, which are nearly insoluble or very sparingly soluble in alcohol at the ordinary temperature,[5] in that it is *readily soluble* in alcohol.

The solubility of most oils and fats in absolute alcohol at 15° C. does not exceed 2 per cent. The solubility in 96 per cent alcohol, or in more dilute alcohol, is smaller still.[5]

Oils and fats containing glycerides of the lower fatty acids, *e.g.* porpoise oil, cocoa nut oil, palm nut oil, and butter fat, are considerably more soluble in alcohol than are those oils and fats which consist chiefly of glycerides of oleic, palmitic, and stearic acids. Triacetin is easily soluble in alcohol. On this behaviour *Mecke*, *Morrschöck*, as also *Arnold*, based a method for the detection of cocoa nut oil and palm nut oil in lard (cp. Vol. II. Chap. XIV. under "Lard," also under "Butter Fat"). On treating such fats as lard, tallow, butter fat with 95 per cent alcohol, the portion dissolved by the alcohol is richer in olein than is the undissolved portion. With regard to the different solubilities of cocoa nut oil and palm nut oil in alcohol as a means of differentiating these oils from each other, see Vol. II. Chap. XIV. "Palm Nut Oil" and "Cocoa Nut Oil." Oils consisting to a great extent of the glycerides of linolic and linolenic acids, as *e.g.* linseed oil, also exhibit a slightly increased solubility in alcohol.

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[1] *Journ. Soc. Chem. Ind.*, 1893, 717; cp. also Klein, *Milchwirthschaftl. Zentralbl.*, 1907 (3), 282.

[2] *Analyst*, 1893, 218.

[3] *Chem. News*, 1861, 230.

[4] O. Corelli, *Inaug. Dissert.*, Zürich, 1909.

[5] Cp. A. J. J. Vandevelde, *Bull. Soc. Chim. Belge*, 1911 (25), 210.

Since the solubility in alcohol does not furnish any discriminating value beyond the identification of castor oil, the determinations published by *Girard* and others need not be enumerated here. Besides, the numbers given by various observers are hopelessly discordant. This may be partly due to the presence of varying amounts of free fatty acids, whereby the solubility in alcohol is considerably increased. Alcoholic solutions of free fatty acids dissolve neutral oils and fats readily; as a rule, oils containing more than 50 per cent of free fatty acids are completely soluble in alcohol.[1] Thus, in the older literature, olive kernel oil was described as soluble in alcohol; it has since been shown that the alleged solubility was solely due to the large proportion of free fatty acids in the samples originally examined. In order to obtain reliable results it would be necessary to carry out determinations with oils and fats freed from free fatty acids. The age of the oils would also have to be taken into account, as oxidised oils (containing glycerides of oxidised acids) are much more soluble in alcohol than are the original glycerides; in this respect they approximate to castor oil. Furthermore, in the presence of notable amounts of lecithin as in the case of egg oil, the solubility of lecithin in alcohol causes the extracted fat to be more readily dissolved by alcohol than it would be, if free from lecithin.

The following data, due to *Cesàro*,[2] deserve recording:—Palmitin, stearin, and olein are almost insoluble in 91 per cent alcohol. At 35° C. myristin is little soluble; laurin is easily soluble, and separates almost completely in the form of crystals, when the solution is cooled down to 13° C. The glycerides of lower carbon contents than laurin remain dissolved at 13° C. By means of alcohol it would therefore be possible to separate the glycerides into three groups, the intermediate group being soluble at 35° C. and insoluble at 13° C. This group contains essentially laurin.

At higher temperatures, the solubility in alcohol increases, and under suitable conditions of pressure and concentration of alcohol, and above a definite temperature, oils and fats form a homogeneous mixture with this menstruum. The temperature at which the mixture will just separate into its component parts is termed by *Crismer* **the critical temperature of dissolution.** (This is analogous to the critical temperature of gases.)

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[1] Macquer showed in 1745 that the cause of the solubility of oils and fats in alcohol was an acid substance (*sc.* fatty acid), and that the solubility increases with the proportion of this substance (*sc.* the free fatty acids).

[2] *Bull. Acad. Roy. Belgique*, 1907, 1004.

Crismer[1] proposed the determination of the critical temperatures of dissolution as a means of differentiating oils and fats, and especially of distinguishing butter fat from those fats that are likely to be used for its adulteration. *Crismer* places a few drops of the oil or melted fat in a glass tube 9 cm. long and 5-6 mm. wide, and adds about twice the volume of 90 per cent alcohol. The tube is then sealed, fixed by means of a platinum wire to the bulb of a thermometer, and heated in a bath of sulphuric acid or glycerin, until the meniscus separating the two layers has flattened to a plane. After heating a little longer, so as to allow the temperature to rise about another 10° C., the thermometer is withdrawn from the bath and rapidly turned up and down several times. It is then replaced in the bath, the source of heat is removed, and the tube observed carefully, whilst the thermometer is gently shaken. The temperature at which a marked turbidity appears, is recorded as the critical temperature.

If the critical temperature does not exceed the boiling point of alcohol (78° C.), an open tube may be used in place of a sealed one. Thus in the case of butter fat, 0·5 c.c. of the filtered fat, with twice its volume of absolute alcohol, is placed in a tube 7 to 8 cm. long and about 1 cm. in diameter. The tube is provided with a cork, fitted with a thermometer, the bulb of which becomes wholly immersed in the liquid on inserting the cork into the tube. The tube is gently heated in a larger tube, which serves as an air- or water-bath, until by agitating the contents a homogeneous liquid is obtained. The mixture is then allowed to cool, and the critical temperature determined as described above.

This method has hitherto been used chiefly by Belgian chemists in the examination of butter (Vol. II. Chap. XIV.).

The critical temperature of dissolution of a mixture is, according to *Crismer*, approximately the arithmetical mean of those of its constituents; it may be calculated from the following formula:—

$$T_m = \frac{nT_a + (100 - n)T_b}{100},$$

where

T_m = the critical temperature of the mixture.
T_a = the critical temperature of the constituent a.
T_b = the critical temperature of the constituent b.
n = the volume of constituent a in 100 volumes.
$100 - n$ = the volume of constituent b in 100 volumes.

From the experiments made hitherto, the further deduction has been derived that substances of the same nature have practically the same critical temperature of dissolution.

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[1] *Bull. de l'Assoc. Belge des Chimistes*, 1895, ix. 71, 143; 1896, ix. 359; x. 312; cp. also *Liége Congrès*, 1905, section i. p. 323.

The critical temperature of dissolution in alcohol of 0·792 specific gravity at 20° C. has been determined by *Cesàro*[1] in the case of the following pure glycerides :—

Butyrin . . .	below	– 10°	C.
Laurin . . .	„	30·0°	„
Myristin . . .	„	40·5°	„
Palmitin . . .	„	56·0°	„
Stearin . . .	„	66·0°	„
Olein . . .	„	70·0°	„

The observations recorded up to the present for natural oils and fats are collated in the following table :—

Critical Temperatures obtained with Alcohol, of specific gravity 0·8195, *at* 15·5° *C.*

Substance.	Number of Samples.	°C.	Observer.
Japanese fish oil .	...	108	Crismer and Motteu[2]
Cotton seed oil .	...	115-116	Herlant[3]
Colza oil . . .	...	132-135	Crismer and Motteu
Sesamé oil . .	...	120·5	Herlant
Arachis oil . .	1	115-116	„
Arachis oil . .	2	123	„
Olive oil . . .	...	123	„
"Animal" oil . .	...	120	Crismer and Motteu
Sheep's foot oil .	...	102	„
Neat's foot oil . .	...	95	„
Lard oil . . .	...	104	„
Apricot kernel oil .	1	47·7	Dieterich
Cacao butter . .	...	126	Crismer
Cocoa nut oil . .	...	71-75	„
Butter fat . .	14	98-102	Crismer
Butter fat . .	4	98-103	Herlant
"Margarine" . .	...	122-126	Crismer
Carnaüba wax . .	...	154	Crismer
Beeswax . . .	from various sources	129-133	„
Ozokerite		175	Crismer
Paraffin wax, according to constitution and melting points		140-160	„
Oil of turpentine		14	„

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[1] *Bull. Acad. Roy. Belgique*, 1907, 1004.

[2] *Journ. Soc. Chem. Ind.*, 1896, 300.

[3] *Ibid.*, 1896, 562.

By using more dilute alcohol, higher values are obtained, as will be seen from the following table, due to *Asbòth* :[1]—

Critical Temperatures with Alcohol, of 90 *per cent by volume, of specific gravity* 0·8332

	Number of Samples.	Becomes perfectly clear at °C.	Commences to become cloudy at °C.	Commences to form 2 layers at °C.	Critical Temperature. °C.
Butter fat .	7	119-134	117·5-131	113·5-120	111·5-115
Butter fat .	1	124	121	116	115
"Margarine"	2	140-151	138-148	135-144·5	133·5-142

If absolute alcohol be employed, an open tube may be used, as stated already. The results obtained for butter fat will be given in Vol. II. Chap. XIV. under " Butter Fat."

The critical temperatures of dissolution in **acetone** have been studied by *E. Louïse and E. Sauvage.*[2] *H. Duperthuis*[3] proposes to use a mixture of **aniline** and **alcohol** (1 : 4).

For the application of the critical temperature to the differentiation of ceresin from paraffin see Vol. III. Chap. XV. " Ceresin."

Valenta[4] classifies oils and fats into three groups according to their solubility in **acetic acid**. The test is carried out by thoroughly mixing equal volumes of oil or fat and glacial acetic acid, of specific gravity 1·0562, in a test-tube, and warming the mixture, in case no solution has taken place in the cold.

1*st Group.*—Completely soluble at the ordinary temperature (14° to 20° C.) : Castor oil.

2*nd Group.*—Completely soluble, or nearly so, at temperatures ranging from 23° C. up to the boiling point of glacial acetic acid : Pumpkin seed oil, cotton seed oil, sesamé oil, apricot kernel oil, almond oil, arachis oil, olive oil, cod liver oil, laurel oil, mowrah seed oil, palm oil, nutmeg butter, cacao butter, palm nut oil, cocoa nut oil, bone fat, beef tallow, butter fat, beef stearine.

3*rd Group.*—Not completely dissolved at the boiling point of glacial acetic acid, the oils belonging to the " Rape Oil Group " :—Rape seed oil, mustard seed oil, hedge mustard oil, etc.

The oils belonging to the second group may be further differentiated by gradually warming the sample with an equal volume of glacial acetic acid with frequent shaking until complete solution is effected. A thermometer is then introduced into the liquid, and the temperature is noted at which turbidity appears. According to *Valenta,* the fats of the second group may be subdivided into two classes: the one embracing the following fats—palm oil, laurel oil, nutmeg butter, cocoa nut oil, palm nut oil, and mowrah seed oil; the remaining oils of that group form the second class. The temperatures found by *Valenta* are given in the following table.

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[1] *Chem. Zeit.*, 1896, 685.

[2] *Compt. rend.*, 1907, 145, 183 ; cp. also Louïse, *Compt. rend.*, 1909 (149), 284 ; *Ann. des Falsific.*, 1911, 302.

[3] *Mitth. a. d. Geb. der Lebensm. u. Hygiene*, 1911 (2), 65.

[4] *Journ. Soc. Chem. Ind.*, 1884, 643.

Allen's [1] and *Hoton's* [2] observations, however, are not in agreement with those recorded by *Valenta*, as will be seen from the following table. Nor do the numbers given by *Hoton* agree in every case with those found by *Allen* :—

Solubility of Fatty Oils and Solid Fats in Acetic Acid

Kind of Oil or Fat.	Temperature of Turbidity for equal Volumes of Oil or Fat and Glacial Acetic Acid spec. grav. 1·0562.		
	Valenta	Allen.	Hoton.
	°C.	°C.	
Linseed oil	...	57-74	
Niger seed oil	...	49	
Pumpkin seed oil	108		
Cotton seed oil	110	90	75-85
Sesamé oil	107	87	87
Apricot kernel oil	114		
Almond oil, sweet	110		
Arachis oil	112	87	93
Yellow olive oil	111		
Green olive oil (of second expression)	85		
Menhaden oil	...	64	
Cod liver oil	101	79	
Shark liver oil	...	105	
Seal oil	...	72	
Whale oil	...	38, 86	
Porpoise oil	...	40	
Neat's foot oil	...	102	
Laurel oil	26-27	40	
Mowrah seed oil	64·5		
Palm oil	23	83	
Nutmeg butter	27	39	
Cacao butter	105	Insoluble	
Palm nut oil	48	32	
Cocoa nut oil	40	7·5	7·5
Lard	...	96·5	102
Bone fat (American)	90-95		
Beef tallow	95		
Oleomargarine	...	96·5	
Butter fat	...	61·5	40-55 [3]
Tallow stearine (m. p. 55·8° C.)	114		
Sperm oil	...	98-103	
Arctic sperm oil	...	102	98-105
,, ,,	...	...	92-95

The following table, comprising oils belonging to *Valenta's* third group, more clearly brings out the same point :—

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[1] *Journ. Soc. Chem. Ind.*, 1886, 69 ; 282.

[2] *Bull. de la Soc. Chim. de Belgique*, 1904, 2.

[3] Twelve samples.

Kind of Oil.	Specific Gravity at 15·5° C. (water at 15·5=1).	Observer.		
		Valenta.	Allen.	Hurst. Temp. of Turbidity.
				°C.
Rape . .	0·9145	Insoluble	Insoluble	88
Rape . .	0·9168	,,	,,	86
Rape . .	0·9132	,,	,,	85
Rape . .	...	,,	,,	73
Colza . .	0·9162	,,	,,	99
Colza . .	0·9131	,,	,,	97
Colza . .	...	,,	,,	94
Colza . .	...	,,	,,	94
Colza . .	0·9132	,,	,,	82

Thomson and Ballantyne,[1] experimenting with acetic acids of different strengths, arrived at the following numbers :—

Kind of Oil	Free Acid calculated as Oleic Acid.	Temperature of Turbidity with Glacial Acetic Acid of		
		Sp. Gr. 1·0542.	Sp. Gr. 1·0552.	Sp. Gr. 1·0562.
	Per cent.	°C.	°C.	°C.
Olive oil (Gioja) . . .	9·42	65	80	91
Same oil, freed from free acid	none	87	...	...
Olive oil (Syrian) . .	23·88	42	...	...
Olive oil	5·19	78	96	...
	3·86	85	100	111
Arachis oil (commercial) .	6·20	76	92	112
Arachis oil (French, refined)	0·62	96	114	Not completely dissolved
Rape oil	2·43	110	Not completely dissolved	...
	4·54	105	...	...
Linseed oil	0·76	61	78	90
Linseed oil (Baltic) . .	3·74	42	59	71
Linseed oil (East India) .	0·79	57	...	...
Linseed oil (River Plate) .	1·21	56	...	...

The figures of the last table prove that the amount of free fatty acid in fats considerably influences the indications of *Valenta's* test.

Notwithstanding these serious discrepancies, *Valenta's* test may, in conjunction with other tests, afford some valuable hints in the examination of an oil.[2]

The following modification of *Valenta's* test was proposed by *Jean* :[3] Place 3 c.c. of the sample in a graduated test-tube of 1 cm. diameter, and immerse the tube in water at 50° C. Remove, by means of a finely drawn-out pipette, so much oil that exactly 3 c.c. remain (at the temperature of 50° C.). Next introduce, by means of a graduated pipette, 3 c.c. of acetic acid, of the specific gravity 1·0565 at 15° C. (prepared from glacial acetic acid by adding the requisite amount of water), measured off at 22° C., warm the contents of the tube in the water for a few minutes, then cork well, and agitate thoroughly. Allow the mixture to settle out at 50° C. until two distinct layers are noticeable, and read off the volume of the undissolved acetic acid. The volume of the acid dissolved in the fat is then easily calculated. *Jean* found the following results for the oils and fats enumerated in the table :—

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[1] *Journ. Soc. Chem. Ind.*, 1891, 233.

[2] Cp. also E. W. Pollard, *Pharm. Journ.*, 1908 (27), 361.

[3] *Corps gras industriels*, 1892 [19], 4.

Kind of Oil or Fat.	Acetic Acid (sp. gr. 1·0565 at 15° C.) dissolved. Per cent.
Arachis oil (Boulam)	41·65
Arachis oil (Gambia)	43·66
Colza oil	30·00
Ravison oil	33·30
Almond oil, sweet	33·00
Olive oil	35·00
Walnut oil	36·60
Cameline oil	36·60
Castor oil	100·00
Maize oil	100·70
Beech nut oil	53·3
Poppy seed oil (Indian)	63·3
Poppy seed oil (French)	43·3
Neat's foot oil	43·3
Sheep's foot oil	36·66
Horse fat	30·08
Lard	26·66
Veal tallow	26·66
Butter, 9 samples of different origin	63·33 [1]
Cotton seed stearine	40·00
" Butterine "	31·60
" Margarine "	26·66
Palm oil	100·00
Cocoa nut oil	100·00

For further information the reader must be referred to the monograph on " Butter Fat," Vol. II. Chap. XIV.

Hoton [2] resumed the study of the solubility of glycerides in acetic acid, but no decisive results have been obtained hitherto. It need, therefore, only be stated that when using acetic acid of 1·057 specific gravity at 15° C. (containing 90·25 per cent of glacial acetic acid) *Hoton* found that cotton seed oil dissolved 20 per cent of acetic acid at 20° C., butter fat 40 per cent at 30° C., and " margarine " 20-25 per cent of acid at 30° C., whereas cocoa nut oil, if kept above its melting point, dissolved any proportion.

The behaviour of some oils with carbolic acid was studied by *Salzer*.[3] He adds the oil drop by drop, with constant shaking, to 10 c.c. of an

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[1] Besides these nine samples, all of which gave 63·33 per cent, two abnormal butters were examined, giving 58·7 and 73·0 respectively.

[2] *Bull. Soc. Chim. de Belgique*, 1904 [18], 147 ; 1912 (26), 70 ; cp. *Revue Internat. Falsific.*, 1905 [18], 85.

[3] *Arch. d. Pharm.*, 227, 433.

87 per cent phenol solution (prepared from 373 grms. of crystallised phenol and 56·7 grms. of water [1]) contained in a graduated cylinder, until the turbidity persists. (In liquefied phenol of a higher strength than 91 per cent, most oils seem to be equally soluble; important differences only appear when employing weaker solutions.) In the following table *Salzer's* results are reproduced :—

Kind of Oil.	Dissolved by 10 c.c. of a Solution containing Phenol.		
	91 per cent.	87 per cent.	83 per cent.
	c.c.	c.c.	c.c.
Almond oil	...	Min. 2·5 Max. 3·5	
Olive oil	...	Min. 2·0 Max. 3·0	
Rape oil	4	...	
Linseed oil	...	...	3
Poppy seed oil	...	6·8	Min. 2
Croton oil	16	8·5	4·0
Arachis oil	11·5	4·8	0·8
Cotton seed oil	10·5	5·5	1·0
Sesamé oil	10	3·8	0·8
1 part of olive oil + 1 pt. of poppy seed oil	...	4·8	
3 parts of olive oil + 1 pt. of poppy seed oil	...	3·4	
3 parts of olive oil + 1 pt. of arachis oil	...	3·0	
1 part of olive oil + 1 pt. of arachis oil	...	3·8	
9 parts of olive oil + 1 part of rape oil	...	2·1	
Croton oil	...	Distinct turbidity with 2·3	

Salzer claims to be able thus to detect adulterants in almond oil, cod liver oil, etc. The figures recorded in the table are not, however, such as will inspire confidence in this method; moreover, free fatty acids increase the solubility. *Salzer's* method can, therefore, at best only serve as a preliminary test.

The solubilities of some fats in benzene as determined by *Dubois and Padé* are given in the following table :—

Solubility of Solid Fats in Benzene

Kind of Fat.	100 grms. of Benzene dissolve at 12° C.
	Grms.
Mutton tallow	14·70
Beef tallow	15·89
Veal tallow	26·08
Lard	27·30
Butter fat	69·61
Margarine	12·83

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[1] This solution was first suggested by Crook (*Zeits. f. analyt. Chem.*, 19, 369).

With regard to the behaviour of oils to dimethylsulphate cp. Chap. IX.

The thorough study of the solubilities of oils and fats for the purpose of analysis is still a desideratum. No doubt the tediousness of "solubility methods" has hitherto deterred investigators from an exhaustive inquiry. Hence attention had been directed to the more promising problem of studying the solubilities of the fatty acids with a view to analytical separation (see Chap. VIII.) and their salts. Thus the study of solubilities in alcohol of the potash soaps of different oils and fats was made by *Freundlich*[1] (cp. also "Solubilities of the lead soaps in common ether and petroleum ether," *G. B. Neave*, Chap. III. p. 142).

The use of esters to phthalic acid as a fat solvent, proposed by *A. Hesse*,[2] therefore deserves attention.

11. Electrical Conductivity

The determination of the electrical conductivity was proposed by *Palmieri*[3] as a means of detecting adulterants in olive oil. For this purpose a special apparatus termed "diagometer" was constructed.

Later on, *A. Bartoli*[4] made an extensive examination of the electrical conductivity of oils and fats. The main results arrived at are as follows: The conductivity of an oil increases with the rise of temperature; its amount varies, however, with the nature of the oil. Drying oils, when exposed to the air, acquire a greater conductivity than non-drying oils. An increase, though to a smaller extent, is also observed in the case of non-drying oils, when they have become rancid. A table, arranged according to the magnitude of the electrical conductivity, begins with olive oil and ends with linseed oil.

Solid fats, with the exception of lard, exhibit an increase of conductivity at temperatures from 170° to 220° C. Nutmeg butter is characterised by a sudden increase at the temperature of its melting point. A similar table of conductivities for the solid fats opens with chicken fat and closes with nutmeg butter.

The measurement of the electrical conductivity of the potash soaps obtained by saponifying an oil or fat was proposed by *L. Herlant*.[5] It is of course essential to employ in each case the same amount of fat and alkali, and to dilute the solutions to exactly the same strength, as also to make all observations at one and the same temperature. For the examination, 10 grms. of an oil or fat are mixed in a flask with 45 c.c. of normal alcoholic potash and saponified by heating for thirty minutes on the water-bath, under a reflux condenser. The alcoholic soap solution is then made up to 250 c.c. with distilled water and electrolysed.

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[1] *Chem. Revue*, 1908, 135; 160.

[2] German patent 227,667.

[3] *Rend. della Acc. di Napoli*, 1881.

[4] *Il nuovo Cimento*, 1890, tomo 28, 25.

[5] *Journ. Soc. Chem. Ind.*, 1896, 562.

The resistance which a cube having a side of 1 cm., filled with the solution, offers is termed the *specific resistance* r of this solution, and its inverse ratio $\frac{1}{r}$ expresses its *specific conductivity.* For practical purposes, comparison is made with the specific conductivity of a $\frac{1}{500}$ normal solution of potassium chloride, for which $\frac{1}{r} = 0{\cdot}002244$ at 18° C. If K be a coëfficient depending on the trough, then we have for the potassium chloride solution $\frac{1}{r}K = 0{\cdot}002244$, and for the specific conductivity of any other solution in this trough $l = \frac{1}{rl} + K$.

The numbers obtained by *Herlant* are given in the following table. A few values for butter fat and "margarine" are added here, as *Herlant* believes that this method may be useful in the examination of butter. The third and fourth columns are added in order to show that the conductivity stands in direct relation to the refractive index and the critical temperature :—

Oil or Fat.	Specific Conductivity at 18° C.	Refractive Index. Degrees in Zeiss's Butyro-refractometer at 35° C.	Critical Temperature of Dissolution. ° C.
Cotton seed .	0·008629	63	115-116
Arachis I. . .	0·008700	58·25	115-116
,, II. .	0·008741	60·25	123
Sesamé . .	0·008779	63	120·5
Olive . .	0·009927	57·25	123
Butter fat 1 .	0·006157	98-103	44·5
,, 2 .	0·006500		45
,, 3 .	0·006507		45
,, 4 .	0·007010		48
Margarine 1 .	0·008221	122 123	52·5
,, 2 .	0·008459		56·5
,, 3 .	0·008472		54
,, 4 .	0·008489		58

12. Calorimetric Examination

The calorimetric examination of oils and fats is not likely to find application in practical work, as the meagre information furnished thereby is out of all proportion to the labour involved in making the determination. It will be gathered from the following tables that this method is incapable of yielding such definite information as is readily obtained by a number of methods which can be carried out in a much shorter time without requiring the use of complicated apparatus.

With regard to the difference between fresh and rancid fats in the calorimetric examination, cp. p. 58.

Heats of Combustion of Fatty Acids

Acid.	Calories per Gram.	Observer.
Acetic	206·7	Stohmann[1]
Butyric (normal) . .	520·4	"
Valeric (normal) . .	677·2	"
Caproic	830·2	"
Caprylic	1138·7	Louguinine[2]
Capric	1458·3	Stohmann[1]
Lauric	1771·8	"
"	1759·7	Louguinine
Myristic	2085·9	"
"	2061·8	Louguinine[2]
Palmitic	2398·4	Stohmann[1]
"	2371·8	Louguinine[2]
Stearic	2711·8	Stohmann[1]
Arachidic	3025·8	"
Behenic	3338·3	"
Erucic	3297·2	"
Brassidic	3290·1	"
Behenolic	3255·1	"
Dihydroxybehenic . .	3235·5	"

Heats of Combustion of Glycerides

	Per 1 Gram-Molecule Constant Volume.	Observer.
Trilaurin	5707·0	Stohmann
"	5707·4	Louguinine
Trimyristin . . .	6650·5	Stohmann, etc.
"	6607·9	Louguinine
Dierucin	6979·5	Stohmann
Trierucin	10265·5	Stohmann, etc.
Dibrassidin . . .	6953·7	"
Tribrassidin . . .	10236·0	"

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[1] Stohmann and collaborators (Kleber, Langbein, and Offenhauer), *Journ. f. prakt. Chem.*, 1885 (31), 297 ; 1890 (42), 367.

[2] *Compt. rend.*, 1886 (102), 1240.

[TABLE

Heats of Combustion of Natural Oils, Fats, and Waxes

Oil or Fat.	Calories per Gram.		
	Constant Volume.	Constant Pressure.	Observer.
Linseed (1900)	9364	9379	Sherman and Snell[1]
,, (1898)	9379	9394	,,
,, (several years old)	9215	9230	,,
Boiled linseed	8810	8824	,,
Poppy seed	9382	9397	,,
Maize (1900)	9413	9428	,,
,, (1898)	9436	9411	,,
,, (crude)	9419	9434	,,
Cotton seed I.	9396	9411	,,
,, II.	9401	9416	,,
,, III.	9390	9405	,,
,, IV. (crude)	9397	9412	,,
,, V.	9336	9351	,,
,, VI. (old)	9323	9328	,,
,, VII. (very old)	9168	9183	,,
Sesamé	9395	9410	,,
Rape I.	9489	9504	,,
,, II.	9462	9477	,,
,, III.	9412	9427	,,
Castor I.	8863	8877	,,
,, II.	8835	8849	,,
Almond I.	9454	9469	,,
,, II.	9311	9326	,,
Arachis	9412	9427	,,
Olive I.	9457	9472	,,
,, II.	9451	9466	,,
Cod liver (fresh)	9437	9452	,,
,, (old)	9277	9292	,,
Shark liver (refined)	9360	9375	,,
,, (crude)	9371	9386	,,
Whale	9473	9488	,,
Cacao butter	9460	...	Langbein[2]
Cocoa nut	9005	...	,,
Goose	9503	...	Stohmann
Lard	9469	...	,,
,, (1900)	9451	9466	Sherman and Snell
,, (1899)	9447	9462	,,
,, (four to five years old)	9394	9409	,,
,, (three years old)	9372	9387	,,
Beef	9485	...	Stohmann
Mutton	9492	...	,,
Butter	9503	...	,,
Spermaceti	9946	9961	Sherman and Snell

With regard to the heat of combustion of beeswax cp. Vol. II. Chap. XIV. "Beeswax."

The specific heat of a fat can be calculated, according to *Kopp's* law, from its elementary composition. This may be illustrated by the case of stearin, which for 76·85 per cent of carbon, 12·36 per cent of hydrogen, and for 10·79 per cent of oxygen, gives the following atomic proportions: Carbon $\frac{76\cdot85}{12} = 6\cdot57$; Hydrogen $\frac{12\cdot36}{1} = 12\cdot36$; Oxygen $\frac{10\cdot79}{16} = 0\cdot67$. Hence the specific heat is $(6\cdot57 \times 1\cdot8 =)11\cdot83 + (12\cdot36 \times 2\cdot3 =)28\cdot43 + (0\cdot67 \times 4\cdot0 =)2\cdot68 = \frac{42\cdot94}{100} = 0\cdot4294$. The molecular heat, *i.e.* the product of the molecular weight and specific heat, is the sum of the atomic heats of the elements in the molecule (where C has 1·8, H 2·3, and O 4·0).

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[1] *Journ. Amer. Chem. Soc.*, 1901, 164.

[2] *Zeit. f. angew. Chem.*, 1908, 1070.

The latent heat of fusion is of importance when it is required to calculate the heat units to be abstracted on cooling an oil, *e.g.* in the manufacture of "winter oils." Whereas in the case of water the latest heat of fusion can be calculated from the specific heat, this cannot be done in the case of fats and waxes, as they do not melt suddenly but soften gradually, so that the exact points at which they are still solid or already liquid cannot be ascertained.

In the case of fats and waxes the specific heat varies considerably with the temperature. When they commence to soften, the specific heat increases suddenly very much, for part of the heat of fusion is used up for internal work, the softening representing the commencement of melting. Thus tristearin has at 6° C. the fairly constant specific heat of 0·336. This is increased at 10°, 20°, 30°, and 40° C. to 0·397, 0·409, 0·449, and 0·501, and at 50° C. is 0·510. At 50° to 55° C. the edges of small particles of tristearin begin to soften, and the specific heat quickly rises to 1·3-1·4. Palmitin shows a similar curve, the specific heat varying from 0·330 at −7° C. to 0·478 at +60° C., and more than 1 at 3° to 4° C. below the melting point, viz. 66·5° C. Other fats behave in the same manner.

The determination of the specific heat of fats is in *Vandevyer Grau's*[1] opinion, if not impossible, at least extraordinarily difficult, as the latent heat of fusion causes an elevation of temperature. He gives the following observations:—

Olive oil at 6·6° C.	0·471
Castor oil at 6·6° C.	0·434
Beeswax at −21° to +3° C.	0·429
Beeswax at 65° to 100° C.	0·499
Palmitic acid at 65° to 104° C.	0·653

The latent heat of fusion of paraffin wax is recorded as 39 calories (*Graefe*) and 35 (*Batelli*).

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[1] *Ann. Chim. Anal.* **5**, 321.

CHAPTER VI

CHEMICAL METHODS OF EXAMINING OILS, FATS, AND WAXES—QUANTITATIVE TESTS

SINCE the natural oils and fats represent complex mixtures, in varying quantities, of the simple and, as it appears, chiefly, mixed glycerides of the different fatty acids enumerated in Chapter III., complete fat analysis should embrace the isolation of each individual fatty acid and of the foreign substances dissolved in the oils and fats. The attempt to detect and identify all the individual fatty acids in a fashion similar to that in which the individual elements are detected in an inorganic substance must, however, in the present state of our knowledge, be abandoned as a hopeless task in technical analysis (cp. Chap. XII.).

The same remarks apply to the examination of waxes.

Although in the examination of oils, fats, and waxes we are not yet able to obtain results which are accurate in a strictly scientific sense, a number of methods answering very satisfactorily the requirements of technical analysis have been evolved.

These methods consist in ascertaining certain numbers—" values " —which depend on the nature of the various fatty acids, the proportion of admixed substances, the presence of free fatty acids and (or) alcohols, etc.

The " values " obtained by the methods to be described in this chapter furnish a measure of the quantity of the acids, alcohols, etc., without, however, in each case fixing their absolute quantity. These methods have, therefore, been appropriately termed by *Hübl* " **quantitative reactions.**"

Besides the " quantitative reactions " we have at our disposal a number of chemical reactions which are usefully applied to the examination of fatty substances, such as the elaïdin test, oxygen and ozone absorption test, bromide test, etc.

Hitherto these methods have not been worked out so fully as to admit of their being classed amongst the quantitative reactions, although in all probability some of them (ozone absorption) will attain to that rank. Meanwhile we must look upon them as preliminary tests that can be usefully employed as sorting tests, or as confirmatory tests in those cases where the interpretation of the quantitative methods leads to ambiguous conclusions. These preliminary tests or " **qualitative reactions** " will be described in the following chapter (Chap. VII.).

Further insight into the composition of the natural oils, fats, and waxes is gained by examining the *isolated fatty acids.* The methods employed for this purpose will be dealt with in Chapter VIII.

The methods which are applied to the examination of insoluble alcohols (such as are obtained on saponifying waxes), and, in general, to the unsaponifiable matter found in oils, fats, and waxes, will be detailed in Chapter IX.

In this chapter the quantitative reactions will be considered.

QUANTITATIVE REACTIONS

I subdivide the numbers—" values "—obtained with the aid of the quantitative reactions into two classes :—

A. Characteristics.
B. Variables.

In the earlier editions of this work I used for Class A the denomination " constants," but as this term has been frequently interpreted in too literal a sense, and has even been compared with " true constants of nature," it appears preferable to substitute for it the expression " characteristics," indicating the fact, that although the numbers are specific for each kind of fat or wax, they still allow of certain fluctuations within narrow limits.

Under " characteristics " I shall comprise those numbers which depend entirely on the specific nature of an oil, fat, or wax, and hence assist most materially in identifying a given oil, fat, or wax.

The " variables " [1] furnish numbers which allow us to judge of the *quality* of a given oil, fat, or wax. These numbers naturally vary with the state of purity, rancidity, age, etc., of the given oil, fat, or wax.

The *characteristics* will be considered under the following heads :—

(1) Saponification Value.
(2) (Bromine or) Iodine Value.
(3) *Reichert* (*Reichert-Meissl* or *Reichert-Wollny*) Value.
(4) Titration number of Insoluble Volatile Acids.

The *variables* will comprise :—

(1) Acid Value.
(2) Amount of Glycerol, expressed in per cent.
(3) Diglycerides and Monoglycerides.
(4) Amount of Unsaponifiable Matter, expressed in per cent.

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[1] Cp. *The Laboratory Companion to Fats and Oils Industries,* Macmillan, 1901, p. 6.

Midway between the two classes stands the *acetyl value*, which in some cases must be considered a " characteristic," whereas in other cases it is a " variable."

A. CHARACTERISTICS

1. Saponification Value[1]

The saponification value indicates the number of milligrams of potassium hydrate required for the complete saponification of one gram of a fat or wax ; in other words, *it represents the amount of potassium hydrate, expressed in tenths per cent, requisite to neutralise the total fatty acids in one gram of a fat or wax.*

For the determination of the saponification value are required — (1) An accurately standardised hydrochloric acid solution, the titer of which is expressed in terms of KOH ; it is most convenient to use half-normal acid ; (2) an alcoholic potash solution prepared by dissolving about 40 grms. of caustic potash, pure from alcohol,[2] in a little water, and making up the solution with strong alcohol (of a specific gravity not exceeding 0·810) to 1000 c.c. The alcoholic solution is allowed to stand for one day, and is then carefully decanted or syphoned off if a precipitate should appear.[3] The solution should be protected from variations of temperature, but need not be protected from light if the materials used in its preparation are pure.

The alcohol used for preparing the potash solution should be pure ; on treating with a strong solution of caustic potash it should remain colourless. If the alcohol turns yellow immediately, it must be rejected. Alcoholic potash prepared from pure materials will not become dark brown even after several months' standing ; it assumes, however, in course of time, a light yellow colouration, which does not interfere with the accuracy of the titration.[4] Dark solutions should not be used, as they are apt to vitiate the results, especially in the case of drying oils.

Methylated spirit may be used in many cases, but it must be purified as described p. 103. Since methylated spirit contains small quantities of mineral oil (introduced with the denaturant) due care must be

[1] This value is also known as Köttstorfer Value (cp. *Zeits. f. analyt. Chem.*, 1879, 199 ; 431). Before Köttstorfer's method was published, it had been customary in the Marseilles works to express the amount of alkali required for 5 grms. of fatty acids in terms of cubic centimetres of normal alkali (*C. Ferrier*).

[2] It should be noted that caustic potash sticks are sometimes coated by the manufacturer with soft paraffin wax ; cp. F. Bengen, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1910 (19), 269.

[3] The precipitate consists chiefly of potassium carbonate. It may be useful to note that 100 c.c. of half-normal alcoholic potash prepared with 94 per cent alcohol by volume dissolve, at 16° to 18° C., 0·038 grms. of potassium carbonate (Holde, *Chem. Revue*, 1907, 107).

[4] Cp. Siegfeld, *Chem. Zeit.*, 1908, 63 ; Zetsche, *ibid.*, 1908, 222 ; Halla, *ibid.*, 1908, 890.

observed in case the determination of the saponification value be combined with that of the unsaponifiable matter.

The saponification value is determined as follows: Weigh off accurately, in a flask holding 150 to 200 c.c., 1·5 to 2 grms. of the purified and filtered sample. Next run into the flask 25 c.c. of an approximately semi-normal alcoholic solution of caustic potash, measuring it off by means of a pipette. It is not necessary to add exactly 25 c.c., but care must be taken that for each determination precisely the same volume is used. A good plan is to allow the contents of the pipette to run out somewhat rapidly, and to drain until two or three more drops have run off. Then attach a long cooling tube or an inverted condenser to the flask, and heat on the boiling water-bath for half an hour so that the alcohol is kept simmering; in order to accelerate saponification, the contents should at intervals be mixed by imparting to the flask a rotary motion. This treatment will, in the case of most fats and oils, lead to complete saponification. In the case of waxes, especially beeswax, it is necessary to boil the contents of the flask over a flame for at least one hour (cp. Chap. II. p. 107, and Vol. II. Chap. XIV. "Beeswax"). Wool wax, even under these conditions, is not completely saponified, and it is advisable to carry out the test with sodium alcoholate, as described p. 107. When the saponification is deemed to be complete, allow to cool a little, add 1 c.c. of a 1 per cent phenolphthalein solution, and titrate back the excess of potash with the half-normal hydrochloric acid. In case too much alcohol has been volatilised, it is advisable to add some alcohol (previously neutralised, see Chap. II. p. 104), or to titrate with normal acid at first and finish the titration with half-normal acid.

It is recommended to make a blank test by treating the same amount of alcoholic potash in exactly the same manner [1] as is done with the sample. Every source of error, *e.g.* carbonic acid, etc., has therefore, as nearly as possible, the same influence on the final result in both tests, and is thus eliminated. The difference between the numbers of c.c. of acid used in the blank test and in the actual test corresponds to the quantity of potash required for saponification; this is calculated to milligrms. of potash for 1 grm. of fat or wax.

Sulphuric acid should not be substituted for hydrochloric acid, as potassium sulphate is precipitated, whereby the delicacy of the end reaction is impaired.

For *Henriques'* method of cold saponification cp. p. 106.

In the case of dark-coloured solutions, *McIlhiney* [2] proposed to measure the alkali used by the amount of ammonia it will liberate from an ammonium salt. He proceeds as follows: The substance (2 grms.) is saponified with an excess of alcoholic caustic soda, and the alcohol evaporated off. 250 c.c. of 93 per cent alcohol are added next, the soap is dissolved by warming, and carbon dioxide passed through the solution for about one hour, in order to precipitate the excess of alkali as carbonate and bicarbonate. The precipitate is then filtered off, the alcohol evaporated, and 100 c.c. of a 10 per cent solution of ammonium chloride added; the solution is then heated, to distil off the liberated ammonia, which is received in hydrochloric acid and titrated. A correction must, of course, be made for the sodium bicarbonate dissolved by the 93 per cent alcohol. This process is cumbersome and certainly introduces errors; it is far simpler to dilute the soap solution with sufficient alcohol, so as to obtain a distinct end reaction. If need be, the titration may be carried out in a flat porcelain dish, after sufficient dilution with strong alcohol. (*De Negri and Fabris* recommend to use in such cases alkali-blue as an indicator.)

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[1] This should extend also to the material of the flask. Cheap German flasks are attacked by alkali to a considerable extent. It is best to use flasks made of Bohemian or of Jena glass.

[2] *Journ. Soc. Chem. Ind.*, 1895, 197.

Example.—Weighed off 1·532 grms. of olive oil, and saponified with 25 c.c. of alcoholic potash solution. Required for titrating back 12·0 c.c. half-normal acid; further, required for the blank test 22·5 c.c. half-normal acid. Therefore a quantity of caustic potash corresponding to

$$\frac{(22{\cdot}5 - 12{\cdot}0)\ 0{\cdot}0561}{2} \text{ grms.} = 294{\cdot}5 \text{ milligrms. KOH}$$

was employed for saponification. Hence

$$\text{Used for 1 grm. of fat } \frac{294{\cdot}5}{1{\cdot}532} \text{ milligrms. KOH} = 192{\cdot}2 \text{ milligrms. KOH.}$$

The saponification value of the sample of olive oil is therefore 192·2.

Allen[1] proposed to calculate the number of grams of fat saponified by one equivalent of potassium hydrate, *i.e.* by 56·1 grms. of KOH, or, what amounts to the same, by one litre of a normal solution of caustic potash or caustic soda.

The number obtained by dividing the percentage of potassium hydrate required for saponification into 5610 was termed the *saponification equivalent.*

No advantage is gained by expressing this important value in the manner proposed by *Allen*, and I shall therefore adhere in this work to the "*saponification value*" as defined above, in order to avoid confusion. The relation between the *saponification value* and *Allen's saponification equivalent* is shown by the following formulæ:

$$\text{Sap. Val.} = \frac{\text{c.c. of normal potash} \times 56{\cdot}1}{\text{grms. of fat employed}} = \frac{\text{c.c. of normal potash} \times 56100}{\text{milligrms. of fat employed}}$$

$$\text{Sap. Equiv.} = \frac{5610}{\text{per cent KOH}} = \frac{5610}{\dfrac{\text{c.c. of normal potash} \times 0{\cdot}0561}{\text{grms. of fat employed}} \times 100}$$

$$= \frac{\text{grms. of fat employed} \times 5610}{\text{c.c. of normal potash} \times 5{\cdot}61}$$

$$= \frac{\text{grms. of fat employed} \times 1000}{\text{c.c. of normal potash}}$$

$$= \frac{\text{milligrms. of fat employed}}{\text{c.c. of normal potash}};$$

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[1] *Commercial Organic Analysis*, ii. 40.

or, if *a* be the number of c.c. of normal potash, and *b* the number of milligrms. of fat employed :

$$\text{Sap. Val.} = \frac{a}{b} \times 56100\text{; Sap. Equiv.} = \frac{b}{a}.$$

Hence it is evident that the "saponification equivalent" can be found by dividing 56100 by the saponification value ; conversely, the saponification value is obtained by dividing 56100 by the saponification equivalent :

$$\text{Sap. Val.} = \frac{56100}{\text{Sap. Equiv.}}\text{; Sap. Equiv.} = \frac{56100}{\text{Sap. Val.}}$$

An easy calculation will show that the saponification value and the saponification equivalent are identical for the number $236{\cdot}87 = \sqrt{56100}$.

The saponification values of neutral glycerides and other esters of fatty acids vary, of course, with the nature of the fatty acids ; the lower the molecular weight of the fatty acids (or, what amounts to the same, of the esters) the more potash will be required to neutralise the fatty acids of 1 grm. of fat or wax, or, in other words, the higher will be the saponification value. To illustrate this more clearly, I subjoin in the following tables the saponification values of some pure triglycerides, diglycerides, and monoglycerides, as also of some waxes (esters of monohydric alcohols).

[TABLE

Saponification Values of Triglycerides

Triglyceride.	Formula.	Molecular Weight.	Saponific. Value.
Simple Triglycerides—			
Acetin	$C_3H_5(O.C_2H_3O)_3$	218	772·0
Butyrin	$C_3H_5(O.C_4H_7O)_3$	302	557·3
Valerin	$C_3H_5(O.C_5H_9O)_3$	344	489·2
Caproin	$C_3H_5(O.C_6H_{11}O)_3$	386	436·1
Caprylin	$C_3H_5(O.C_8H_{15}O)_3$	470	358·1
Caprin	$C_3H_5(O.C_{10}H_{19}O)_3$	554	303·7
Laurin	$C_3H_5(O.C_{12}H_{23}O)_3$	638	263·8
Myristin	$C_3H_5(O.C_{14}H_{27}O)_3$	722	233·1
Palmitin	$C_3H_5(O.C_{16}H_{31}O)_3$	806	208·8
Hydnocarpin	$C_3H_5(O.C_{16}H_{27}O)_3$	794	211·9
Stearin	$C_3H_5(O.C_{18}H_{35}O)_3$	890	189·1
Olein	$C_3H_5(O.C_{18}H_{33}O)_3$	884	190·4
Linolin	$C_3H_5(O.C_{18}H_{31}O)_3$	878	191·7
Chaulmoogrin	$C_3H_5(O.C_{18}H_{31}O)_3$	878	191·7
Linolenin	$C_3H_5(O.C_{18}H_{29}O)_3$	872	193·0
Clupanodonin	$C_3H_5(O.C_{18}H_{27}O)_3$	866	194·3
Ricinolein	$C_3H_5(O.C_{18}H_{33}O_2)_3$	932	180·6
Arachin	$C_3H_5(O.C_{20}H_{39}O)_3$	974	172·7
Erucin	$C_3H_5(O.C_{22}H_{41}O)_3$	1052	160·0
Cerotin	$C_3H_5(O.C_{26}H_{51}O)_3$	1226	137·3
Melissin	$C_3H_5(O.C_{30}H_{59}O)_3$	1394	120·7
Hydroxystearin	$C_3H_5(O.C_{18}H_{35}O_2)_3$	938	179·4
Dihydroxystearin	$C_3H_5(O.C_{18}H_{35}O_3)_3$	986	170·7
Trihydroxystearin	$C_3H_5(O.C_{18}H_{35}O_4)_3$	1034	162·8
Sativin	$C_3H_5(O.C_{18}H_{35}O_5)_3$	1082	155·0
Linusin	$C_3H_5(O.C_{18}H_{35}O_7)_3$	1178	142·4
Mixed Triglycerides—			
Acetodiformin	$C_3H_5(O.C_2H_3O)(O.COH)_2$	190	885·8
Acetodibutyrin	$C_3H_5(O.C_4H_7O)(O.C_2H_3O)(O.C_4H_7O)$	274	614·3
Myristopalmitoölein	$C_3H_5(O.C_{14}H_{27}O)(O.C_{16}H_{31}O)(O.C_{18}H_{33}O)$	804	209·3
Oleodipalmitin	$C_3H_5(O.C_{16}H_{31}O)_2(O.C_{18}H_{33}O)$	832	202·3
(Dipalmitoölein) Stearodipalmitin	$C_3H_5(O.C_{16}H_{31}O)_2(O.C_{18}H_{35}O)$	834	201·8
(Dipalmitostearin) Oleopalmitostearin	$C_3H_5(O.C_{16}H_{31}O)(O.C_{18}H_{33}O)(O.C_{18}H_{35}O)$	860	195·7
(Stearopalmitoölein) Palmitodistearin	$C_3H_5(O.C_{18}H_{35}O)_2(O.C_{16}H_{31}O)$	862	195·2
(Distearopalmitin) Oleodistearin	$C_3H_5(O.C_{18}H_{33}O)(O.C_{18}H_{35}O)_2$	888	189·5
Elaïdodistearin	$C_3H_5(O.C_{18}H_{33}O)(O.C_{18}H_{35}O)_2$	888	189·5
Dioleostearin	$C_3H_5(O.C_{18}H_{33}O)_2(O.C_{18}H_{35}O)$	886	189·9

[TABLE

Saponification Values of Diglycerides

Diglyceride.	Formula.	Molecular Weight.	Saponification Value.
Diacetin	$C_3H_5(OH)(O\,.\,C_2H_3O)_2$	176	637·6
Dibutyrin	$C_3H_5(OH)(O\,.\,C_4H_7O)_2$	232	483·7
Divalerin	$C_3H_5(OH)(O\,.\,C_5H_9O)_2$	260	431·5
Dicaproin	$C_3H_5(OH)(O\,.\,C_6H_{11}O)_2$	288	389·6
Dicaprylin	$C_3H_5(OH)(O\,.\,C_8H_{15}O)_2$	344	326·2
Dicaprin	$C_3H_5(OH)(O\,.\,C_{10}H_{19}O)_2$	400	280·5
Dilaurin	$C_3H_5(OH)(O\,.\,C_{12}H_{23}O)_2$	456	246·1
Dimyristin	$C_3H_5(OH)(O\,.\,C_{14}H_{27}O)_2$	512	219·1
Dipalmitin	$C_3H_5(OH)(O\,.\,C_{16}H_{31}O)_2$	568	197·6
Distearin	$C_3H_5(OH)(O\,.\,C_{18}H_{35}O)_2$	624	179·8
Diolein	$C_3H_5(OH)(O\,.\,C_{18}H_{33}O)_2$	620	181·0
Dilinolin	$C_3H_5(OH)(O\,.\,C_{18}H_{31}O)_2$	616	182·1
Dilinolenin	$C_3H_5(OH)(O\,.\,C_{18}H_{29}O)_2$	612	183·3
Diricinolein	$C_3H_5(OH)(O\,.\,C_{18}H_{33}O_2)_2$	652	172·1
Diarachin	$C_3H_5(OH)(O\,.\,C_{20}H_{39}O)_2$	680	165·0
Dierucin	$C_3H_5(OH)(O\,.\,C_{22}H_{41}O)_2$	732	153·3
Dicerotin	$C_3H_5(OH)(O\,.\,C_{26}H_{51}O)_2$	848	132·3
Dimelissin	$C_3H_5(OH)(O\,.\,C_{30}H_{59}O)_2$	940	119·1
Dihydroxystearin	$C_3H_5(OH)(O\,.\,C_{18}H_{35}O_2)_2$	656	171·1
Didihydroxystearin	$C_3H_5(OH)(O\,.\,C_{18}H_{35}O_3)_2$	688	163·1
Ditrihydroxystearin	$C_3H_5(OH)(O\,.\,C_{18}H_{35}O_4)_2$	720	155·9
Disativin	$C_3H_5(OH)(O\,.\,C_{18}H_{35}O_5)_2$	752	149·2
Dilinusin	$C_3H_5(OH)(O\,.\,C_{18}H_{35}O_7)_2$	816	137·5
Of Acid having Mol. Wt. 276	$C_3H_5(OH)(O\,.\,R)_2(R=259)$	608	184·5

Saponification Values of Monoglycerides

Monoglyceride.	Formula.	Molecular Weight.	Saponific. Value.
Monoacetin	$C_3H_5(OH)_2(O\,.\,C_2H_3O)$	134	428·7
Monobutyrin	$C_3H_5(OH)_2(O\,.\,C_4H_7O)$	162	346·3
Monovalerin	$C_3H_5(OH)_2(O\,.\,C_5H_9O)$	176	318·8
Monocaproin	$C_3H_5(OH)_2(O\,.\,C_6H_{11}O)$	190	295·3
Monocaprylin	$C_3H_5(OH)_2(O\,.\,C_8H_{15}O)$	218	257·3
Monocaprin	$C_3H_5(OH)_2(O\,.\,C_{10}H_{19}O)$	246	228·1
Monolaurin	$C_3H_5(OH)_2(O\,.\,C_{12}H_{23}O)$	274	204·7
Monomyristin	$C_3H_5(OH)_2(O\,.\,C_{14}H_{27}O)$	302	185·8
Monopalmitin	$C_3H_5(OH)_2(O\,.\,C_{16}H_{31}O)$	330	170·0
Monostearin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{35}O)$	358	156·7
Monoölein	$C_3H_5(OH)_2(O\,.\,C_{18}H_{33}O)$	356	157·58
Monolinolin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{31}O)$	354	158·5
Monolinolenin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{29}O)$	352	159·4
Monoricinolein	$C_3H_5(OH)_2(O\,.\,C_{18}H_{33}O_2)$	372	150·9
Monoarachin	$C_3H_5(OH)_2(O\,.\,C_{20}H_{39}O)$	386	145·3
Monoerucin	$C_3H_5(OH)_2(O\,.\,C_{22}H_{41}O)$	412	136·2
Monocerotin	$C_3H_5(OH)_2(O\,.\,C_{26}H_{51}O)$	470	119·3
Monomelissin	$C_3H_5(OH)_2(O\,.\,C_{30}H_{59}O)$	526	106·6
Monohydroxystearin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{35}O_2)$	374	150·0
Monodihydroxystearin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{35}O_3)$	390	143·9
Monotrihydroxystearin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{35}O_4)$	406	138·2
Monosativin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{35}O_5)$	422	133·0
Monolinusin	$C_3H_5(OH)_2(O\,.\,C_{18}H_{35}O_7)$	454	123·6
Of Acid having Mol. Wt. 276	$C_3H_5(OH)_2(OR)(R=259)$	350	160·3

Saponification Values of Waxes

Wax.	Formula.	Molecular Weight.	Saponific. Value.
Cetyl palmitate, cetin	$C_{16}H_{33}.O.CO.C_{15}H_{31}$	480	116·9
Octodecyl palmitate	$C_{18}H_{37}.O.CO.C_{15}H_{31}$	508	110·4
Ceryl palmitate	$C_{26}H_{53}.O.CO.C_{15}H_{31}$	620	90·5
Melissyl palmitate, myricin	$C_{30}H_{61}.O.CO.C_{15}H_{31}$	676	83·0
Cetyl stearate	$C_{16}H_{33}.O.CO.C_{17}H_{35}$	508	110·4
Ceryl cerotate	$C_{26}H_{53}.O.CO.C_{25}H_{51}$	760	73·8
Cocceryl coccerate, coccerin	$C_{30}H_{60}.(O.C_{31}H_{61}.O_{2})_{2}$	1382	81·2
Cholesteryl palmitate	$C_{27}H_{45}.O.CO.C_{15}H_{31}$	624	89·9
Cholesteryl oleate	$C_{27}H_{45}.O.CO.C_{17}H_{33}$	650	86·3
Cholesteryl stearate	$C_{27}H_{45}.O.CO.C_{17}H_{35}$	652	86·0
Isocholesteryl stearate	$C_{27}H_{45}.O.CO.C_{17}H_{35}$	652	86·0
Cholesteryl cerotate	$C_{27}H_{45}.O.CO.C_{25}H_{51}$	764	73·4
Melissyl melissate	$C_{30}H_{61}.O.CO.C_{29}H_{59}$	872	64·3
Psyllostearyl psyllostearylate	$C_{33}H_{67}.O.CO.C_{32}H_{65}$	956	58·6

The preceding tables refer to neutral substances only, that is, to glycerides and waxes which are devoid of free fatty acids.

Since the natural oils, fats, and waxes contain certain amounts of free fatty acids, depending on the state of purity of the specimen of oil, fat, or wax under examination, it cannot be expected that different samples of one and the same kind of oil, fat, or wax will always have the same saponification value. Although the saponification values are characteristic numbers, as the following table shows, they should not be considered as applying within very strictly defined limits to every specimen of the same kind. For, in the first instance, certain fluctuations must occur, which depend on the proportion of free fatty acids. These fluctuations will, as a rule, be small, since, to take an example, the amount of caustic potash required to saponify 100 parts of stearin differs by only 5 per cent from the amount of caustic potash required to neutralise 100 parts of stearic acid. This is clearly brought out by the following table :—

Variation of Saponification Value with the Amount of Free Fatty Acids

Stearin. Per cent.	Stearic Acid. Per cent.	Saponification Value.	Neutralisation Value.
100	0	189·1	0
75	25	191·02	49·37
50	50	193·30	98·75
25	75	195·41	148·13
0	100	197·5	197·5

Besides the proportion of free fatty acids, natural conditions, such as climate and difference of soil in the case of a plant, and race and age in the case of an animal, cause the saponification value to vary somewhat.

Saponification Values of Oils, Fats, and Waxes

Oil.	Class.	Group.	Saponification Value.
Perilla	Drying oils		189·6
Linseed . . .			192-195
Tung			193
Lallemantia . . .			185
Candle nut . . .			192·6
Stillingia . . .			210·4
White acacia . .			192·4
Cedar nut . . .			191·8
Garden rocket . .			191·8
Hemp seed . . .			192·5
Burdock . . .			196·6
Gynocardia . . .			198·3
Nsa-Sana . . .			191·6
Walnut, Nut . .			195
Arbutus unedo . .			208
Linaria . . .			188·6
Safflower . . .			186·6-193·3
Kaya			188·4
Inukaya . . .			188·5
Echinops . . .			189·6
Soya bean . . .			193
Poppy seed . . .			195
Amoora . . .			189·7
Manihot . . .			188·6
Melia azedarach . .			191·5
Croton Elliotianus .			201·5
Henbane . . .			170·8
Millet seed . . .			183·8
Niger seed . . .			190·2
Sunflower . . .			193·5
Yellow acacia . .			190·6
Para rubber tree seed .			206·1
Service berry . .			208·0
Celosia . . .			190·5
Argemone . . .			189
Fir seed . . .			191·3
Pine nut . . .			192·8
Madia			192·8
Strawberry seed . .			193·7
Raspberry seed . .			192·3
Hawthorn seed . .			172·8
Red currant seed . .			189
Blackberry seed . .			189·5
Tobacco seed . .			190

Saponification Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Saponification Value.
Cameline	Semi-drying oils	Cotton seed oil group	188
Grape seed			179 ; 190
Celandine			198·2
Daphne			196·5
Clover, red			189·9
,, white			189·5
Pumpkin seed			188·4
Water melon			189·7
Melon seed			193·3
Maize (corn)			188-193
Persimmon seed			188
Wheat			188·5
Datura			186
Beech nut			193·5
Kapok			181-196·5
Cotton seed			193-195
Sesamé			189-193
Basswood			178·1
Lemon pips			188·4
Luffa seed			187·8
Myrtle seed			199·8
Ikpan seed			194·0
Anis seed			178·3
Croton			210-215
Zachun			194·1
Curcas, purging nut			193·2
Brazil nut			193·4
Mucuna			178·22
Sorghum			172·1 (?)
Tomato seed			183·6
Spindle tree			230·1
Garden cress		Rape oil group	178-183
Ravison			174-179
Hedge mustard			174
Rape (colza)			170-179
Black mustard			174
White mustard			170-174
Radish seed			173-178
Jamba			172·3
Small fennel	Non-drying oils		196·4
Quince			181·8
Cherry kernel			194
Cherry laurel			194
Apricot kernel			192·5
Plum kernel			191·5
Peach kernel			192·5
Almond			191·0
Wheat meal			166·5 (?)-182·8
Sanguinella			192·1
Acorn			199·3

Saponification Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Saponification Value.
Californian nutmeg	Non-drying oils		191·3
Owala			168·4
Arachis			190-196
Rice			193·2
Tea seed (Chinese)			195·5
Tea seed (Assam)			194·0
Tsubaki			180·9-192·6
Sasanqua			193·6
Njore-Njole			193·1
Pistachio			191·3
Hazel nut			192·0
Koëme			196
Elderberry			209·3
Elozy			155·3 (?)
Staff tree			223·5 (?)
Olive			185-196
Olive kernel			183
Calophyllum			196·2
Coffee berry			175 (?)
Ungnadia			191·5
Ben			184-187
Strophantus			187·9-194
Senega root			193·8
Sterculia			187·9
Paradise nut			173·6
Secale			178·4-191·4
Canari			193·9
Birch seed			211
Oleander			202·5
Terminalia (Myrobalan)			193-206
Castor		Castor oil group	183-186
Menhaden	Marine animal oils	Fish oils	190·6
Japanese sardine			189·8-196·2
Salmon			182·8
Herring			171-194
Sturgeon			186·3
Cramp fish			148·2 (?)
Sunfish			147·6 (?)
Cod liver		Liver oils	171-189
Haddock liver			188·8
Skate liver			185·4
Shark liver			161·0
Coal fish liver			177-181
Ling			184·1
Seal		Blubber oils	189-196
Whale			188·0-194
Turtle			209-211·3

Saponification Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Saponification Value.
Dugong . . .	Marine animal oils	Blubber oils	197·5
Dolphin (body) . .			197·3-203
Dolphin (jaw) . .			290
Porpoise (body) . .			195
Porpoise (jaw) . .			254-272
Brown fish . . .			224·8
Chrysalis . . .	Terrestrial animal oils		192
Egg			184·4-190·2
Sheep's foot . . .			194·7
Horses' foot . . .			195·9
Neat's foot . . .			194·3-199
Oil or Fat.			
Chaulmoogra . .	Vegetable fats	Chaulmoogra oil group	213
Hydnocarpus . .			207
Lukrabo . . .			210
Parkia		Laurel oil group	184·5
Pongam . . .			178-183·1
Laurel			197·9-210
Carapa			195·6
Nux Vomica . .			166·2-170·6
Baobab . . .			190·3
Margosa . . .			196·9
Niam			195·6
Kadam seed . . .			197·6
Inukusu . . .			241·39
Mowrah seed . .			188-194
Illipé butter . .			188·4
Njave			182-185·3
Aouara . . .		Palm oil group	196·8
Palm			196-205
Gamboge butter . .			196·4
Akee			194·6
Macassar . . .			221·5
Sawarri . . .			199·51
Mafura tallow . .			200-221
Phulwara butter . .			190·8
Nutmeg butter . .		Myristica group	199·6
Ucuhuba . . .			219·5
Ochoco . . .			238·5
Shea butter . . .		Cacao butter group	179-192
Surin			179·5
Mkányi . . .			190·5
Rambutan tallow. .			193·8

Saponification Values of Oils, Fats, and Waxes—continued

Oil or Fat.	Class.	Group.	Saponification Value.
Malabar tallow			188·7-192
Cacao butter			193·55
Vegetable tallow			200·3
Kokum butter			187-191
Borneo tallow			192·4-196
Muriti		Cocoa nut oil group	246·2
Mocaya			240·6
Cohune			253·9-255·3
Maripa			259·5-270·5
Aouara kernel			242·9
Palm nut			242-250
Cocoa nut			246-260
Cocos acrocomoides			292·8
Tonka butter			257
Dika		Dika fat group	214·5
Tangkallak			268·2
Cáy-Cáy			235·3
Kusu			283·8
Japan wax			217-237·5
Myrtle wax			208·7
Icebear	Animal fats	Drying fats	187·9
Rattlesnake			210·9
Blackcock		Semi-drying fats	201·6
Lynx			190·2
Wild duck			198·5
Marmot			197·1
Horse			195-197
Hare			200·9
Rabbit (wild)			199·3
Rabbit (tame)		Non-drying fats	202·6
Horse marrow			199·8
Goose (domestic)			193·1
Goose (wild)			196
Chicken			193·5
Human, adult			195
Lard			195·4
Wild boar			195·1
Dog			195·4
Wild cat			199·9
Domestic cat			190·7
Beef marrow			199
Bone			190·9-195
Beef tallow			193·2-200

Saponification Values of Oils, Fats, and Waxes—continued

Fat.	Class.	Group.	Saponification Value.
Mutton tallow	Animal fats	Non-drying fats	192-195·2
Elk			195·1
Reindeer			194·7
Roebuck			199·0
Fallow buck			195·6
Stag			199·9
Butter		Milk fats	220-233
Waxes.			
Sperm oil	Liquid waxes		123-147
Arctic sperm oil			123-135·9
Carnaüba wax	Solid waxes	Vegetable waxes	79-95
Pisang wax			109
Flax wax			101·5
Wool wax		Animal waxes	102·4
Beeswax			90-98
Spermaceti			123-135
Insect wax			80·5-93

A consideration of the foregoing numbers shows that the waxes are characterised by low saponification values, so that these numbers alone afford a ready means of differentiating waxes from oils and fats.

It will further be seen that the majority of oils and fats have saponification values lying in the neighbourhood of 193. In the case of unknown samples, *wide* deviations from this number in either direction will at once enable the analyst to single out individual oils or fats.

Thus, oils belonging to the rape oil group are characterised by a considerably lower saponification value, viz. about 175. The lower saponification values of these oils find their explanation in the large proportion of erucin they contain. Similarly, castor oil may be differentiated from the bulk of the other oils by its lower saponification values, due to the presence of ricinoleic acid.

On the other hand, large deviations in the opposite direction enable us to single out a number of oils and fats, and hence render their recognition a comparatively easy task. Thus the high saponification values of the fluid portion of dolphin and porpoise oils are indicative of a high proportion of the lower fatty acids. A prominent example of a characteristically high saponification value is that of butter fat, so that by the saponification value alone, butter fat can be differentiated from margarine. High saponification values are characteristic of fats containing preponderantly myristic acid, and especially of the members of the cocoa nut oil and dika fat groups.

It should be noted that the preceding remarks as to the indications furnished by the saponification value refer to unadulterated oils, fats, and waxes, *i.e.* to commercial samples which may contain a smaller or larger amount of free fatty acids, as also small amounts of unsaponifiable matter. If mineral oils or other unsaponifiable substances are intermixed with the fatty substances, then, naturally, the indications furnished by the saponification values alone, if considered without further investigation, would be entirely misleading, since the unsaponifiable matter naturally depresses the saponification value. Thus, to take an example, an oil having the saponification value 193, if adulterated with 10 per cent of mineral oil, would show a saponification value of about 175, and might, therefore, be mistaken for a rape oil, if no further tests were applied.

Again, if colophony (rosin) be dissolved in the fatty substance, the saponification value will remain unaffected, if rosin of about the same saponification value be used; with a rosin of a somewhat lower saponification value, the saponification value of the mixture would, of course, be somewhat depressed.

2. (Bromine or) Iodine Value

The (bromine or) iodine value indicates the percentage of (bromine or) iodine chloride absorbed by a fat or wax, expressed in terms of (bromine or) iodine.

This value is a measure of the proportion of unsaturated fatty acids, which, both in their free state and in combination with glycerol, have the property of assimilating halogens with formation of saturated compounds.

Theoretically, the acids belonging to the oleic and ricinoleic series should absorb two atoms of chlorine, bromine or iodine, or one molecule of iodochloride. Hence the glycerides of these acids should absorb six atoms of chlorine, bromine or iodine, or three molecules of iodochloride. Similarly the acids of the linolic series should assimilate four atoms of halogens or two molecules of iodochloride; the members of the chaulmoogric series should assimilate two atoms of halogens or one molecule of iodochloride; the members of the linolenic series six atoms of halogens or three molecules of iodochloride; and the members of the clupanodonic series eight atoms of halogens or four molecules of iodochloride.

Whilst these theoretical postulates are borne out by experiments in the case of oleic, ricinoleic, linolic, chaulmoogric, linolenic, and clupanodonic acids, it appears that this rule only applies to doubly linked carbon atoms. Trebly linked pairs of carbon atoms should, theoretically, absorb with equal facility four atoms of chlorine, bromine, iodine, or two molecules of iodochloride. Experience has, however, shown (Chap. III. p. 145) that only two atoms are readily absorbed.

In the case of chlorine and bromine two molecules can be added by allowing the action to last a prolonged time, especially if this action be assisted by catalysts (ferric chloride, etc.) and exposure to light. In the case of iodine and iodochloride only one molecule of halogen is absorbed. This behaviour would seem to constitute a most characteristic means of differentiating the acids of the linolic series from the isomeric acids of the stearolic series (see Chap. III. p. 202).

Obviously the preparation of products containing chlorine, absorbed solely by a process of addition, is attended with more difficulty than that of bromo-, iodo-, or iodochloro-addition products; hence in technical analysis only bromine and iodine—the latter in the form of iodochloride—are employed.

Bromine Value

If dry bromine is allowed to act on an oil, it is absorbed with a more or less violent reaction, and evolution of hydrobromic acid takes place. The reaction must therefore be moderated by previously dissolving both the bromine and the oil in a suitable solvent.

The determination of **bromine absorption** values was first proposed by *Cailletet* (1857); the application of this method to the analysis of fats is, however, due to *Mills*[1] and his collaborators *Snodgrass* and *Akitt.*

Mills proceeds as follows:—0·1 grm. of an oil or fat, dried thoroughly and filtered, is dissolved in 50 c.c. of carbon tetrachloride placed in a narrow-mouthed stoppered bottle of 100 c.c. capacity. To this solution is added a standard carbon tetrachloride solution of bromine (about 0·006-0·008 grm. per c.c.) until after the lapse of fifteen minutes the colouration persists. The excess of bromine can be measured either by comparing the colouration with that similarly produced in a blank experiment, or, more accurately, by titrating back with a standard solution of β-naphthol in carbon tetrachloride, when monobromonaphthol is formed. The bromine absorbed is calculated to 100 grms. of fat. The average probable error is stated to be 0·46 per cent.

Mills laid the greatest stress on the necessity of rigidly excluding moisture, since the bromine absorption number is found too high in the presence of water; therefore aqueous solutions of bromine must not be used. Carbon tetrachloride was substituted for carbon bisulphide, for the reason that at the ordinary temperature the solution of bromine is more stable in the former solvent than in the latter.[2] Instead of β-naphthol, potassium iodide may be added, and the liberated iodine titrated with sodium thiosulphate.

In the course of the reaction small quantities of hydrobromic acid are formed, due to the substitution of hydrogen by bromine in the

[1] *Journ. Soc. Chem. Ind.*, 1883, 435; 1884, 366.

[2] The following reaction taking place in a solution of bromine in carbon bisulphide should be noted as involving loss of bromine. After several days' standing CS_2Br_4 is formed; this is decomposed by water (moisture) with separation of crystals of $(CBr_3)_2S_3$.—(J. L.)

molecule of the fatty substance. (The hydrobromic acid thus formed can be detected by shaking the product with water and testing the aqueous solution with silver nitrate.)

Thus concurrently with **addition** (*i.e.* absorption of bromine due to bromine being assimilated by one molecule of an unsaturated glyceride, to form a saturated compound), a further quantity of free bromine disappears, owing to the formation of substitution products and hence of hydrobromic acid; therefore the **total absorption** of bromine, as measured by the method described, is due to both **addition** and **substitution.**

The more concentrated the bromine solution employed, the greater is the amount of substitution products formed; it is therefore evident that bromine values obtained by allowing dry bromine to act on an oil are apt to be too high.

A measure of the amount of substitution that has taken place is furnished by the quantity of hydrobromic acid formed. Hence the **true bromine value** would be the difference between the total bromine assimilated and the bromine absorbed by substitution.

M^cIlhiney[1] determines the "bromine addition" and the "bromine substitution" values in the following manner:[2]

From 0·25 to 1·00 grm. of the oil or fat is dissolved in 10 c.c. of carbon tetrachloride in a 500 c.c. stoppered bottle, and an excess of a ⅓ normal solution of bromine in carbon tetrachloride is added. After a few minutes the bottle is placed in ice so that a partial vacuum is produced by the condensation of the vapours. A piece of india-rubber tubing is now slipped over the neck so as to form a well around the stopper. The well is filled with water, which is sucked into the bottle by carefully lifting the stopper. 25 c.c. of water are introduced into the bottle, the contents are well shaken (to effect complete absorption of the hydrobromic acid), and 10-20 c.c. of a 20 per cent solution of potassium iodide and about 75 c.c. more water are added. The iodine liberated by the excess of bromine is measured by titration with standard thiosulphate solution, and calculated to bromine. The total amount of bromine added is ascertained in a blank test; the difference between the two amounts corresponds to the **total bromine absorption.** This is calculated to units per cent of the sample taken.

The contents of the bottle are next transferred to a separating funnel, and the aqueous solution is separated and filtered. If it be blue, it is decolourised by a few drops of thiosulphate solution, and the free acid is determined as hydrobromic acid by titration with decinormal alkali, methylorange being used as an indicator.[3] The bromine calculated from the hydrobromic acid and expressed in per cent of the sample gives the **bromine substitution value.** Twice this number subtracted from the total bromine absorption furnishes the **bromine addition number.**

It is obvious that the substitution number must be doubled, since for each bromine atom converted into hydrobromic acid, there has been removed from the original bromine solution 1 molecule (or 2 atoms of bromine), as is explained by the following equation :—

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[1] *Journ. Soc. Chem. Ind.*, 1894, 668.

[2] Cp. Allen, *Commercial Organic Analysis*, ii. 384.

[3] For another method cp. M^cIlhiney, *Journ. Amer. Chem. Soc.*, 1899, 1084.

$$\underset{\text{Fatty Acid.}}{C_nH_mO_2}+Br_2=\underset{\substack{\text{Bromosubstitution}\\ \text{product.}}}{C_nH_{m-1}O_2Br}+HBr.$$

F. Telle[1] is of the opinion that his method permits to effect complete *addition* of bromine without simultaneously obtaining substitution products. For the details of his method the original paper must be consulted.

A *gravimetric* process for the determination of the bromine value proposed by *Hehner* and (independently) by *Waller*[2] has been shown by *Lewkowitsch*[3] to be unreliable. Whilst in a number of cases (*e.g.* olive oil) the proposed method led to results agreeing with those obtained by *Hübl's* standard method (see below), enormous discrepancies were observed in a number of other cases.[4]

The determination of the bromine value has been wholly superseded by the determination of the **iodine absorption** value according to *Hübl's* and *Wijs'* methods. These methods yield far more constant and reliable results. In fact, the reliability of bromine absorption processes is gauged by comparison with the iodine numbers as found in *Hübl's* and *Wijs'* processes. For this purpose, bromine values are calculated to iodine values by multiplication with $\frac{127}{80}(=1{\cdot}5875)$. It should, however, be distinctly understood that bromine values are not directly convertible into iodine values, since a varying amount of substitution (by bromine) takes place concurrently with absorption, as pointed out already. Therefore, the bromine absorption method should only be resorted to in exceptional cases, such as in the examination of rosin oils (Vol. III. Chap. XV.) or of linseed and boiled oils suspected of being adulterated with rosin oils.

The bromine absorption method has found useful application in the " Bromide Test " (Chaps. VII. and VIII.).

Hübl[5] found that iodine is assimilated by oils and fats only slowly at the ordinary temperature, whilst at higher temperatures[6] the action of iodine becomes very irregular, owing to complicated reactions taking place. He ascertained, however, that from an alcoholic solution of iodine, in the presence of mercury bichloride, glycerides of the unsaturated fatty acids absorb iodine in a very regular, well-defined manner, so that a quantitative method can be based on this reaction. The following solutions are required for **Hübl's process** :—

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[1] *Journ. de Chim. et de Phys.*, 1905, 111, 183.

[2] *Analyst*, 1895, 280. It should be noted that Waller examined olive oil only.

[3] *Journ. Soc. Chem. Ind.*, 1896, 859.

[4] Cp. also Jenkins, *Journ. Soc. Chem. Ind.*, 1897, 193. Procter and Bennett, *ibid.*, 1906, 799.

[5] *Journ. Soc. Chem. Ind.*, 1884, 641.

[6] *Ibid.*, 1894, 616 (Schweitzer and Lungwitz).

1. *Solution of Iodine and Mercury Bichloride*, called hereafter (for brevity) *Iodine Solution.*—This is prepared by dissolving on the one hand 25 grms. of iodine in 500 c.c. of pure 95 per cent alcohol, and on the other hand 30 grms. of mercury bichloride in the same amount of 95 per cent alcohol (filtering this solution if necessary), and mixing the two solutions. The iodine solution undergoes considerable reduction in strength (*i.e.* in free iodine) during the first hours after mixing, and should, therefore, be allowed to stand for twelve to twenty-four hours before use. It is not advisable to use iodine solutions older than twenty-four hours. After that time the iodine solution gradually loses strength and is apt to lead to uncertain results. It is convenient to keep both the iodine and the bichloride solutions in stock separately, and prepare only so much *iodine solution* as is required for a test.

2. *Solution of Sodium Thiosulphate* (hyposulphite).—This is prepared by dissolving about 24 grms. of the crystallised salt in 1000 c.c. of water. It is standardised by the following method (due to *Volhard*):—Weigh off accurately 3·8657[1] grms. of pure potassium bichromate,[2] and dissolve in 1000 c.c. of water. Place in a stoppered bottle 10 c.c. of a 10 per cent potassium iodide solution, and 5 c.c. of hydrochloric acid, and run in exactly 20 c.c. of the bichromate solution from a burette. Since each c.c. of this solution liberates precisely 0·01 grm. of iodine, altogether 0·2 grm. of iodine will be set free. This is titrated by means of the thiosulphate solution as described above. The advantage of this method over the older method of starting from re-sublimed iodine lies in its rapidity, the somewhat laborious and tedious preparation and weighing off of pure iodine being saved. Moreover, the bichromate solution keeps for an indefinite time without alteration, and is always ready for ascertaining the strength of the thiosulphate solution.[3]

3. *Chloroform, or Carbon Tetrachloride.*—These solvents are tested for purity[4] by mixing 10 c.c. with 10 c.c. of the iodine solution, and titrating the free iodine after two or three hours' standing. The amount found should be exactly the same as that contained in 10 c.c. of the iodine solution.—Ether must not be used in place of chloroform, as it very frequently contains hydrogen peroxide, which acts on potassium iodide with liberation of iodine. Benzene, *free from thiophene*,[5] is a suitable substitute for chloroform or carbon tetrachloride. In the case of highly oxidised oils, which are no longer completely soluble in carbon tetrachloride, glacial acetic acid should be employed (cp. Vol. III. Chap. XV. "Solid Linseed Oil").

[1] $O = 16$, $H = 1·008$, $Cr = 52·1$. The weight is calculated from the following equation:—

$$Cr_2O_7K_2 + 14HCl + 6KI = Cr_2Cl_6 + 8KCl + 7H_2O + 3I_2.$$

[2] It is necessary to ascertain its purity, as also the absence of sodium bichromate, by determining its oxidising value.

[3] For a method of standardising by means of BaS_2O_3, cp. Plumpton and Chorley, *Proc. Chem. Soc.*, 1895, p. 38; F. Borde (*Bull. Sciences Pharm.*, 1909 (16), 654) proposes to substitute antipyrine for thiosulphate solution.

[4] Commercial carbon tetrachloride not infrequently contains carbon bisulphide; cp. also p. 393.

[5] Farnsteiner, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898, 529.

4. *Solution of Potassium Iodide.*—This is prepared by dissolving 100 grms. of potassium iodide in 1000 c.c. of water. Commercial potassium iodide frequently contains iodate, which with hydrochloric acid gives free iodine. Such impure iodide may, however, be employed, if accurately measured volumes be used and the liberated iodine be taken into account.

5. *Starch Solution.*—This should be prepared afresh for each analysis by stirring 0·5 grm. of pure starch in 50 c.c. of cold water, and heating to the boiling point with constant stirring.

The determination of the iodine value is carried out as follows:—From 0·15 to 0·18 grm. of a drying or a marine animal oil, 0·2 to 0·3 grm. of a semi-drying oil, 0·3 to 0·4 grm. of a non-drying oil, or 0·8 to 1·0 grm. of a solid fat, are weighed off accurately, and placed in a bottle of 500 to 800 c.c. capacity provided with a well-ground stopper. The fat is dissolved in 10 c.c. of chloroform, or carbon tetrachloride, and 25 c.c. of the iodine solution are run in from a pipette. The pipette should always be emptied in exactly the same manner: this is best done by allowing it to drain, until two or three drops have run out. For larger quantities of substance than those stated above, 50 c.c. must be used. In order to prevent loss of iodine by volatilisation, it is advisable to moisten the stopper with potassium iodide solution. The solvent and the iodine solution should give a clear solution on shaking; otherwise more solvent must be added. The bottle is then allowed to stand in a dark place.[1] Should the deep brown colour of the solution disappear after a short time, another 25 c.c. of the iodine solution must be run in, as an excess of iodine is essential for complete absorption. After two hours the solution must still exhibit a deep brown colour. Most of the iodine is absorbed during the first two hours. The reaction then slows down; it cannot be considered complete before the lapse of six to eight hours in the case of solid fats and non-drying oils, and twelve to eighteen hours in the case of drying oils and marine animal oils. Semi-drying oils require eight to ten hours. After standing for the requisite number of hours, 15 to 20 c.c. of the potassium iodide solution are run in, the liquid is well shaken, and then diluted with 400 c.c. of water.[2] The appearance of a red precipitate of mercuric iodide at this stage would indicate that an insufficient quantity of potassium iodide had been employed; therefore, more must be added. The excess of free iodine, part of which will be in the aqueous solution, the remainder being dissolved in the chloroform, or carbon tetrachloride, is titrated with the thiosulphate solution by running the latter into the bottle until, after repeated agitation, both the aqueous and the chloroform, or carbon tetrachloride, layers are but faintly coloured. A few drops of the starch solution are next added and the titration is then brought to an end. Immediately before or after this titration, 25 c.c. of the original iodine solution are standardised in exactly the same manner. The difference between the two figures, corresponding to absorbed halogen, is calculated in terms of iodine to units per cent of the sample. The number thus found is termed the **iodine value.**

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[1] Cp. S. F. Popoff, *Journ. Russ. Phys. Chem. Soc.*, 1906 (38), 1114.

[2] Cp. Ingle, *Journ. Soc. Chem. Ind.*, 1902, 587, and Harvey, *ibid.*, 1902, 438; cp. also Ingle, *ibid.*, 1904, 422, and 1908, 314.

The values as obtained by *Hübl's* method are quite constant, provided an excess of iodine, not less than the amount actually absorbed, has been employed, and the operations be always carried out under identical conditions. The results do not depend on the concentration, nor on an excess of the mercuric bichloride solution, but it is necessary that for every two atoms of iodine at least one molecule of mercury bichloride be present.

When the titrated solution has stood for some time, it becomes blue again; this is no doubt due to the splitting off of iodine, thus proving that the action of iodine on unsaturated compounds is to some extent a reversible one.[1] However, this change does not in the least interfere with the accuracy of the titration.

Example.—Weighed off 0·3394 grm. of lard, dissolved in 10 c.c. of carbon tetrachloride, added 25 c.c. of iodine solution, which required in a blank experiment 60·9 c.c. of thiosulphate solution, 16·45 c.c. of which were equivalent to 0·2 grm. of iodine. For titrating back the excess of iodine in the experiment there were required 39·6 c.c. of thiosulphate solution. Hence, the absorbed iodine corresponds to $60{\cdot}9 - 39{\cdot}6 = 21{\cdot}3$ c.c. of thiosulphate solution.

Since 16·45 c.c. of thiosulphate solution are equivalent to 0·2 grm. of iodine, 21·3 c.c. correspond to $\frac{0{\cdot}2 \times 21{\cdot}3}{16{\cdot}45} = 0{\cdot}2589$ grm. of iodine. Hence 0·3394 grm. of lard absorbed 0·2589 grm. of iodine, or 100 grms. absorbed $\frac{0{\cdot}2589 \times 100}{0{\cdot}3394} = 76{\cdot}28$ grms. of iodine. The iodine value of the specimen of lard is therefore 76·28.[2]

Hübl's process has been examined by many chemists, and proved itself to be one of the most valuable methods employed in the technical analysis of oils, fats, and waxes. The chemical literature of the last twenty years contains numerous papers by various authors purporting to furnish improvements or modifications of the original method. Most of them refer simply to minor or entirely unimportant points. Some of them even reproduce methods which *Hübl* rejected. With the exception of the important *Wijs* modification (described below) they are omitted here, and the reader must be referred for a short survey of the earlier literature on this subject to the second edition of this work.

It need only be stated that, long before a comprehensive explanation of the reactions taking place in *Hübl's* ingenious process was found, the numbers obtained by his method afforded the most valuable guidance in the examination of oils and fats. *Hübl* himself explained the reaction by assuming that a chloro-iodo-addition compound was formed, he having obtained from oleic acid a saturated fatty substance, to which he ascribed the formula $C_{18}H_{34}ClIO_2$.

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[1] The reaction of bromine on unsaturated compound may be considered, for practical purposes, as non-reversible.

[2] For rapid calculation the logarithms of the factor 0·2 c.c. divided by the number of c.c. of thiosulphate are tabulated in Table No. 11 of the author's *The Laboratory Companion to Fats and Oils Industries*, Macmillan and Co., 1901.

If *Hübl's* view is correct, then theory requires, in the first instance, that saturated fatty acids should have no iodine value; secondly, that pure unsaturated fatty acids should furnish iodine values agreeing with the theoretical numbers.

As regards the first point, I examined a number of pure saturated fatty acids, as also amyl alcohol, with the following result :—

	Iodine Value (100 grms. absorb grms. of Iodine).
Propionic acid	0·66
Butyric ,,	0·36
Isobutyric ,	0·00
Valeric ,,	1·32
Caproic ,,	0·30
Œnanthic ,,	0·00
Caprylic ,,	0·55
Pelargonic ,,	1·83
Capric ,,	0·31
Lauric ,,	1·12
Palmitic ,,	0·13
Stearic ,,	0·20
Cerotic[1] ,,	1·34
Dihydroxystearic acid	0·06
Amyl alcohol	0·00

The iodine values should, of course, have been in all cases nil, but considering the difficulty of satisfactorily purifying the fatty acids named, the result may be accepted as proving the fact that saturated fatty acids have no iodine value.

The second postulate is borne out by the experiments set out in the following table :—

Fatty Acids.	Formula.	Atoms of Iodine required to form a Saturated Compound.	100 Grms. of Acid absorb Iodine.		Observer.
			Theory[2]	Experiment.	
			Grms.	Grms.	
Oleic	$C_{18}H_{34}O_2$	2	90·07	89	Geitel[3]
Elaïdic	$C_{18}H_{34}O_2$	2	90·07	90·54	Saytzeff[4]
Brassidic	$C_{22}H_{42}O_2$	2	75·15	75·34	Saytzeff[5]
Isoerucic	$C_{22}H_{42}O_2$	2	75·15	74·42	Alexandroff and Saytzeff[6]
Cholesterol	$C_{27}H_{46}O$	2	65·8	67·3-68·09	Lewkowitsch[7]

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[1] Commercial acid.

[2] For I = 127.

[3] *Journ. f. prakt. Chem.*, 1888 (37), 59.

[4] *Ibid.*, 1894 (50), 75.

[5] *Ibid.*, 1894 (50), 79.

[6] *Ibid.*, 1894 (49), 61.

[7] *Berichte*, 1892, 66.

It must, however, be pointed out distinctly that it is not permissible to conclude, from the excellent agreement between theory and experiment in the cases recorded in the last table, that substances, other than those mentioned above, having unsaturated linkages also yield the theoretically required iodine values. Thus the author[1] obtained the results recorded in the following table with *Hübl's* solution :—

Substance.	Iodine Value.	
	Theory.	Experiment.
Undecylenic acid . . .	138	121-125
Crotonic acid	295	25-25·9
Fumaric acid	219	nil
Maleïc acid	219	nil
Cinnamic acid	170·9	15·3-16·4
Styracin	191·7	81·9-82·9

G. Ponzio and Gastaldi confirm the above results for crotonic and undecylenic acid. It is, therefore, evident that the position of the double linkage plays an important part in the behaviour of a fatty acid in the iodine absorption test. As stated already on p. 392, the naturally occurring acids conform to the theoretical postulates, which is confirmed by the last but one table; yet from observations by *Ponzio and Gastaldi*[2] the fact becomes apparent that if the double linking is in the α-β position,[3] as in the case of 2-3 hypogæic or 2-3 oleic acid, very low iodine values are obtained if *Hübl's* solution be used according to the above-given directions. Thus 2-3 hypogæic and 2-3 oleic acid gave the iodine values 6·6 and 8·7, instead of 99·8 and 90·07 respectively.

From these and similar results the conclusion must be drawn that it is the position of the double bond in the unsaturated acids that influences the iodine absorption. If the double bond is distant from the carboxyl group, as in ordinary oleic and undecylenic acids, the iodine value is normal, whilst if it is nearer the carboxyl group, as in the case of the other acids in the table given above, the iodine value is lower than the theoretical value. Further experiments showed that by prolonging the time of absorption to seventy hours, 2-3 oleic acid gave an iodine value (of 45·9 by *Hanus'* method) of 86·8 by *Wijs'* method. The absorption was due to addition and not to substitution. It would thus appear that the determination of the iodine value furnishes a means of drawing some conclusions as to the position of the double bond in an unsaturated acid.

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[1] See second edition of this work, p. 176; cp. Henricksen, *Liebig's Annalen*, 336, 323, and Bauer, *Berichte*, 37, 3317; Fahrion, *Zeit. f. angew. Chem.*, 1901, 1226; Wake and Ingle, *Journ. Soc. Chem. Ind.*, 1908, 315.

[2] *Gazz. chim. ital.*, 1912, 42, 92.

[3] For Bougault's method of separating unsaturated α-β fatty acids (of the type $CHR:CH.CO_2H$, and of the type $CH_2:CR.CO_2H$) from β-γ unsaturated acids, by means of iodine and yellow mercuric oxide (nascent hypoiodous acid) the original must be consulted (*Compt. rend.*, 1904 (139), 864).

The author further confirmed that all glycerides and fatty acids which occur in commercial oils, fats, and waxes *do* conform with theory, if treated with the *Hübl* iodine solution according to the directions given above, or with the *Wijs* solution according to the conditions laid down below. According to the author's experience, which extends over many years, the iodine value may be relied upon as one of the safest guides in the technical analysis of fats and waxes.

The apparently capricious results which a number of observers obtained with *Hübl's* method in the case of natural oils and fats were explained by those observers by assuming that, simultaneously with the addition of iodine, or iodochloride, substitution takes place in the glyceride molecule, with formation of hydriodic acid—much in the same way as substitution takes place in the case of bromine with formation of hydrobromic acid (see above). It has, however, been shown by *Wijs* [1] that the free acid found in the solution after absorption had taken place from *Hübl's* iodine solution, was not hydriodic but hydrochloric acid. *Waller* had proved the occurrence of hydrochloric acid before *Wijs*, but he erroneously ascribed its formation to a secondary reaction, namely, the action of free chlorine on the water present.

In this connection it may be pointed out that *Waller* proposed to render *Hübl's* solution more stable by the addition of hydrochloric acid to the iodine solution. A number of iodine determinations carried out by means of *Waller's* solution were published by continental observers; therefore, his *modus operandi* may be briefly described:—*Waller's* solution is prepared by dissolving 25 grms. of iodine in 200 c.c. of strong alcohol on the one hand, and 25 grms. of mercuric chloride in 200 c.c. of strong alcohol on the other, then adding 25 grms. of strong hydrochloric acid, of the specific gravity 1·19, to the latter solution, finally mixing the two solutions, and making up to 500 c.c. with alcohol. It will be noticed that *Waller's* solution does not conform to *Hübl's* direction, that there should be present at least one molecule of mercuric chloride—27·5 grms.—to one molecule of iodine—25·4 grms. It will be further noticed that this solution is about twice as strong as the *Hübl* iodine solution.—Although the numbers obtained by *Waller's* method, in the case of oils and fats, do not deviate widely from the *Hübl* numbers, the method is not free from objection, and will therefore not be further considered in this work.[2] It may, however, be pointed out that in the case of mineral oils, cholesterol,[3] and naphthenic acids,[4] *Waller's* solution yields results which are at complete variance with those obtained by *Hübl's* method.

The next important step in the scientific explanation of the *Hübl* reaction was made by *Ephraim*.[5] He observed that the *Hübl* solution required a much larger amount of sodium thiosulphate after addition of potassium iodide than without it, and concluded therefrom that on mixing the components of the *Hübl* solution there is formed *at once* a substance capable of liberating iodine from potassium iodide.

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[1] *Zeits. f. analyt. Chem.*, 1898, 277.

[2] Cp. also Ingle, *Journ. Soc. Chem. Ind.*, 1902, 587.

[3] Marcusson, *Chem. Zeit.*, 1907, 420.

[4] Schwarz and Marcusson, *Chem. Revue*, 1908, 165.

[5] *Analyst*, 1895, 176.

The chemical change taking place in the iodine solution was expressed by *Ephraim* by the following equation :[1]—

$$HgCl_2 + I_2 = HgClI + ICl.$$

This equation would correspond to *Hübl's* directions, that for 2 atoms of iodine at least 1 molecule of mercuric chloride must be used. A solution of iodine monochloride of the same strength as that of the *Hübl* solution must contain 16·25 grms. in 1000 c.c. A number of experiments carried out with iodine monochloride solution of the specified strength on oleic acid, linseed oil, poppy seed oil, sesamé oil, almond oil, arachis oil, olive oil, and castor oil in the same fashion as is done in *Hübl's* iodine test, furnished results identical with those obtained by *Hübl's* method. *Ephraim* concludes, therefore, that alcoholic solutions of iodine monochloride may be substituted for the *Hübl* solution.

A confirmation of *Ephraim's* views, and of *Waller's* statement regarding the occurrence of hydrochloric acid, is found in *Wijs'*[2] experiments, which led to a satisfactory explanation of the reactions occurring in the *Hübl* solution. The first change taking place on mixing the solutions of iodine and of mercuric chloride is represented by the following equation :—

$$HgCl_2 + 2I_2 = HgI_2 + 2ICl \quad . \quad . \quad . \quad . \quad (1).$$

It must be left an open question whether the action takes place in two stages, as shown by the two equations

$$HgCl + I_2 = HgClI + ICl$$
$$HgClI + I_2 = HgI_2 + ICl,$$

or not.

The equation (1) must be looked upon as representing a state of equilibrium between the four substances, since by dissolving mercuric iodide (HgI_2) in iodine chloride (ICl) solution, a mixture identical with the *Hübl* iodine solution is obtained. Equation (1) should, therefore, rather be considered as representing a reversible reaction, though the colour of the solution would point to a preponderance of the system $HgCl_2 + 2I_2$. Concurrently with this main reaction, the following changes occur :— The iodochloride (ICl) formed reacts with the water contained in the 95 per cent alcohol in the following manner :—

$$ICl + H_2O = HCl + HIO \quad . \quad . \quad . \quad . \quad (2),$$

but this change soon reaches a limit, since the hydrochloric acid (HCl)

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[1] Ephraim states distinctly that this equation must not necessarily be considered as expressing the chemical change quantitatively.

[2] *Journ. Soc. Chem. Ind.*, 1898, 698 ; *Zeits. f. angew. Chem.*, 1898, 291 ; cp. also Skrabal and Buchta, *Chem. Zeit.*, 1909, 1193 : 1911, 658.

thus formed precludes the complete decomposition of the water present. The hypoiodous acid (IOH) is converted into iodic acid and free iodine, thus :—

$$5IOH = IO_3H + 2H_2O + 4I \quad . \quad . \quad . \quad . \quad (3),$$

although very slowly, for the amount of hypoiodous acid (IOH) is, as shown, a limited one. Since, however, the iodic acid will interact with free iodine and the hydrochloric acid (see equation 2) in the solution to form iodochloride (ICl), in the manner expressed by the equation

$$IO_3H + 4I + 5HCl = 5ICl + 3H_2O \quad . \quad . \quad . \quad (4),$$

it will be easily seen that a complicated system of equilibrium will result, the chief components of which are represented by the equation (2). Thus, we can assume in the *Hübl* iodine solution the presence of the following substances :—

$$HgCl_2,\ HgI_2,\ I,\ ICl,\ HCl,\ IOH,\ \text{and}\ IO_3H.$$

On standardising the iodine solution, potassium iodide solution and water are added (see p. 397). The changes then taking place are expressed by the following equations :—

$$ICl + KI = KCl + I_2 \quad . \quad . \quad . \quad . \quad (5),$$
$$HCl + IOH + KI = KCl + H_2O + I_2 \quad . \quad . \quad . \quad (6),$$
$$IO_3H + 5HCl + 5KI = 5KCl + 3H_2O + 3I_2 \quad . \quad . \quad (7).$$

It will thus be seen that, provided no other reaction has taken place, the total amount of iodine originally employed (when preparing the iodine solution) must be found in the blank test as iodine, and further, that the final solution cannot contain free acid, provided the alcohol used was neutral.

Experiments, however, show (see p. 396) that the *Hübl* iodine solution loses free iodine rapidly at first, afterwards more slowly, that the solution turns acid, that the amount of acid formed corresponds exactly to the amount of iodine which has become inactive (has "disappeared"), except in the case of very old solutions, which are found to contain acetic acid. The explanation of these phenomena is given by *Wijs* (in contradistinction to his earlier views, which presupposed an interaction between iodine and alcohol, with formation of hydriodic acid) as follows :—A portion of the hypoiodous acid oxidises the alcohol to aldehyde, as shown in the equation

$$2IOH + C_2H_6O = I_2 + 2H_2O + C_2H_4O \quad . \quad . \quad . \quad (8).$$

The equilibrium of the solution thus having been disturbed, fresh hypoiodous acid must be formed, but owing to the increased amount of hydrochloric acid now present, not quite the full quantity of hypoiodous acid can be formed, notwithstanding the fact that the free iodine, which is liberated according to the last equation, interacts with $HgCl_2$ (present in excess) to form fresh ICl, and consequently fresh hypoiodous and hydrochloric acids.

The oxidation of the alcohol, *the cause of the loss in strength of the iodine solution*, therefore proceeds much more slowly after a certain time, or, in other words, the older the solution the more stable it becomes. The acidity of the solution is, of course, explained by the presence of an excess of hydrochloric acid which does not find sufficient hypoiodous acid to be neutralised according to equation (6). The presence of aldehyde has been proved experimentally,[1] and since aldehyde is readily oxidised, by the oxygen of the air, to acetic acid, the excess of free acid in very old solutions is now easily explained by the slow oxidation of the aldehyde.

From the foregoing notes it would follow that by limiting the amount of hypoiodous acid that can possibly be formed, *e.g.* by excluding water, the *Hübl* solution must become more stable. This logical postulate is confirmed by experiment, if the iodine solution is prepared with absolute alcohol or ethyl acetate.

Again, if the decomposition of iodochloride, as explained in equation (2), be limited, by disturbing the equilibrium through increasing the amount of hydrochloric acid at the outset, the same object must be reached. In fact, this is the theoretical explanation for the greater stability of the *Waller* solution (see above); for sulphuric acid does not produce the same effect,[2] and the colour of the *Hübl* solution is rendered much lighter by the addition of hydrochloric acid. This shows that the reaction represented by equation (2) has been much retarded.

Wijs assumed that the active substance in the *Hübl* iodine solution is hypoiodous acid and not iodine monochloride. In support of his view, he quotes the following three arguments. (1) If iodine monochloride were the active substance, the halogen should be absorbed more rapidly from *Waller's* solution than from *Hübl's*, since iodochloride is present in greater concentration in the former solution than in the latter. But the reverse actually holds good, and this may be explained by the gradual or retarded formation of hypoiodous acid. (2) When a solution of hypoiodous acid (prepared by shaking an alcoholic iodine solution with freshly precipitated mercuric oxide and filtering off) is mixed with an oil, values identical with the *Hübl* iodine numbers are obtained, the absorption being complete after ten seconds (one experiment only is given). (3) On increasing the concentration of hypoiodous acid through addition of iodine, mercuric chloride, and water (which favour the formation of hypoiodous acid), more rapid absorption takes place, whereas it is retarded by those agents which reduce the hypoiodous acid concentration, *e.g.* mercuric chloride and hydrochloric acid.

If *Wijs'* assumption were correct, there should be formed for each molecule of hypoiodous acid which is absorbed by an oil, one molecule of hydrochloric acid. Although *some* acid is found, by no means the full quantity is obtained; therefore *Wijs* is driven to the further, somewhat forced assumption that, taking oleic acid as an example, the reaction proceeds as follows :—

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[1] On shaking an alcoholic solution of iodine with mercuric oxide, aldehyde is formed. Cp. also Bougault, *Compt. rend.*, 1904 (139), 864.

[2] Skrabal and Buchta (*Chem. Zeit.*, 1909, 1195) show that hypoiodous acid is very unstable in a solution of sulphuric acid, whereas it is comparatively stable in dilute aqueous solution.

$$C_{18}H_{34}O_2 + HIO = C_{18}H_{34}O_2I.OH,$$
$$C_{18}H_{34}O_2I.OH + HCl = C_{18}H_{34}O_2ICl + H_2O.$$

It is evident that the final product is the same as would be obtained by assuming that iodochloride is the active substance, and that iodochloride is absorbed as such. In fact, *Wijs*' proposal to substitute for *Hübl's* solution a solution of iodine monochloride in acetic acid (inasmuch as the preparation and the keeping of a solution of hypoiodous acid would offer almost insuperable difficulties), amounts practically to a tacit acceptance of the view that iodochloride is the active agent.

Ingle,[1] in an inquiry into the origin and nature of the free acid which is formed in *Hübl's* reaction, showed that the free acid is neither due to substitution (which had been proved before) nor to the splitting off of hydrochloric acid from the chloro-iodo-addition product, but that the formation of the free acid is caused by the action of water on the chloro-iodo-compound, and that the amount of acid thus formed depends upon the chemical structure of the unsaturated compound, and also on the amount of water present.

The foregoing explanations show that *Hübl* has hit off in a happy and very ingenious manner the conditions most favourable for obtaining values which are in close agreement with theory. It is therefore possible, if a sample contains the glyceride of *one* unsaturated fatty acid of known composition in admixture with glycerides of saturated fatty acids, to calculate the absolute amount of the glyceride of that unsaturated fatty acid. In cases of this kind the following table may be found useful. It will also guide the analyst as to the direction which further investigation must take in the case of samples of unknown composition, when, of course, the proportion of glycerides of unsaturated fatty acids cannot be calculated from the iodine value alone.

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[1] *Journ. Soc. Chem. Ind.*, 1902, 587 ; 1904, 422 ; 1908, 314.

Iodine Values of Unsaturated Fatty Acids and of their Mono-, Di-, and Tri-glycerides (Lewkowitsch)

Acid.	Formula.	Iodine Value[1] of Fatty Acid.	Iodine Value of		
			Monoglyceride.	Diglyceride.	Triglyceride.
Tiglic . . .	$C_5H_8O_2$	254·00	145·98	198·43	225·44
	$C_{12}H_{22}O_2$	128·28	93·38	112·39	120·57
	$C_{14}H_{26}O_2$	112·39	84·67	100·00	106·42
Hypogæic Physetoleic Lycopodic . .	$C_{16}H_{30}O_2$	100·00	77·44	90·07	95·25
Hydnocarpic . .	$C_{16}H_{28}O_2$	100·79	77·91	90·71	95·97
Oleic Elaïdic Isooleic Rapic Petroselinic . .	$C_{18}H_{34}O_2$	90·07	71·35	81·93	86·20
Doeglic Jecoleic . .	$C_{19}H_{36}O_2$	85·81	68·65	78·39	82·29
Gadoleic . . .	$C_{20}H_{38}O_2$	81·93	66·14	75·15	78·72
Erucic Brassidic Isoerucic . .	$C_{22}H_{42}O_2$	75·15	61·65	69·40	72·43
Linolic Millet oil Telfairic Elæomargaric .	$C_{18}H_{32}O_2$	181·42	143·50	164·93	173·58
Chaulmoogric . .	$C_{18}H_{32}O_2$	90·71	71·75	82·47	86·79
Linolenic Isolinolenic (?) Jecoric .	$C_{18}H_{30}O_2$	274·10	216·47	249·02	262·15
Isanic . . .	$C_{14}H_{20}O_2$	461·82	345·57	409·67	436·67
Therapic (?) . .	$C_{17}H_{26}O_2$	387·78	302·38	350·34	369·90
Clupanodonic . .	$C_{18}H_{28}O_2$	368·11	290·29	334·21	351·96
Ricinoleic Isoricinoleic Ricinelaïdic Ricinic . .	$C_{18}H_{34}O_3$	85·23	68·28	77·91	81·76
Mixed Triglycerides—					
Myristopalmitoölein	...	...	...	...	31·59
Oleodipalmitin .	...	...	...	...	30·53
Oleopalmitostearin .	...	...	...	...	29·53
Oleodistearin . .	...	...	...	...	28·60
Elaïdodistearin .	...	...	...	...	28·60
Dioleostearin . .	...	...	...	...	58·00

In the case of stearolic and behenolic acids and their glycerides, only one molecule of iodochloride is absorbed, as will be seen from the following table giving the experimental results found by *Quensell.*[2]

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[1] The atomic weight of iodine has been taken as 127.

[2] *Berichte*, 1909, 2445.

		Iodine Value of Fatty Acids.	Iodine Value of		
			Monoglyceride.	Diglyceride.	Triglyceride.
Stearolic .	$C_{18}H_{32}O$	91·2	71·49	82·31	86·35
Behenolic .	$C_{22}H_{40}O$	74·4	61·6	68·92	73·2

Wijs' Modification of Hübl's Process

Wijs' iodine solution is prepared by dissolving separately 7·9 grms. (the correct figure is 7·9617) of iodine trichloride,[1] and 8·7 grms. (the correct figure is 8·6670) of iodine in glacial acetic acid on the water-bath, taking care that the solutions do not absorb moisture. The two solutions are then poured into a 1000 c.c. flask, and the flask is filled up to the mark with glacial acetic acid. A cheaper way of preparing the solution (which commends itself in a laboratory where a large number of iodine tests are made) is to dissolve 13 grms. of iodine in a litre of glacial acetic acid, then to determine accurately its content of iodine, and to pass washed and dried chlorine gas through the solution, until the titration number of the original iodine solution is doubled. A little experience will readily show when this point is reached, as a very distinct change of colour takes place when all the iodine has been converted into iodine monochloride. The glacial acetic acid must be pure, and should be tested by heating with potassium bichromate and concentrated sulphuric acid; even after prolonged standing a green tinge should not be noticeable.[2]

As commercial chloroform frequently contains some alcohol, carbon tetrachloride should be used to dissolve the sample. The carbon tetrachloride must also be tested, with potassium bichromate and concentrated sulphuric acid, for the presence of any oxidisable substance. The solvents should be examined, as directed on p. 396.

In all other respects, including the excess of iodochloride, the test is carried out in exactly the same manner as *Hübl's* iodine test, with this important difference, however, that it is not necessary to allow the solution to stand as long a time as is required in the case of *Hübl's* test. In fact, in the case of oils and fats having an iodine value below 100, half an hour is quite sufficient for the completion of the reaction. Semi-drying oils require about one hour, drying oils and marine animal oils two to six hours according to the unsaturation of the glycerides.

Wijs' solution possesses the further great advantage over *Hübl's* solution in that it keeps its "strength" unchanged for a considerable length of time. In fact, I can testify from my own experience that solutions kept for five months did not appreciably change their "strength." Hence, in ordinary work a blank test is not required in each case, and the determination of the iodine value can be carried out almost as rapidly as the determination of the saponification value.

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[1] Iodine trichloride is considered by some chemists not to be the simple molecular compound ICl_3 but to be better represented by the formula $ICl \cdot Cl_2$. (Cp. Skrabal and Buchta, *Chem. Zeit.*, 1909, 1194.)

[2] Some commercial preparations of glacial acetic acid contain formic acid.

Wijs[1] showed that with his solution, pure fatty acids yield numbers agreeing completely with theory, as is shown by the following table :—

Acid.	Experiment.	Theory.
Erucic acid	74·9	75·15
Brassidic acid	75·0	75·15
Elaidic acid	90·0	90·07
Undecylenic acid	133·1	139
Oleic acid, commercial	87·6	90·07

Furthermore, the author[2] has shown that the iodine numbers of natural oils and fats (and of their fatty acids) as obtained with *Wijs'* solution, agree perfectly with those derived by *Hübl's* method, provided the latter be carried out with all the precautions detailed above.

The author can therefore thoroughly recommend *Wijs'* process. It will be found preferable to the *Hübl* iodine solution in almost every case, as it is infinitely superior to the latter as regards stability. It can be prepared rapidly, and the time spent on the test is very much shortened.

A drawback inherent to *Wijs'* solution is that it is acid ; hence in those not very frequent cases in which it is desirable to avoid the presence of acetic acid, the *Hübl* method will still be used. The *Hübl* method would also be preferred if it be desired to determine the substitution value (if any) as well as the addition value. It should further be noted that in some cases, as in the case of rosin oils and cholesterol, the *Wijs* solution gives very much higher values and, moreover, more capricious results than the *Hübl* method. A minor drawback is that the solution crystallises at 15° C. ; it is therefore advisable to keep the solution in a moderately warm place or to thaw it carefully, if it has solidified.

In addition to the original papers quoted already, the reader may be referred to those mentioned in the footnote.[3] *Hanus*,[4] following a suggestion made by *Bellier*,[1] recommends the substitution of iodine chloride by iodine bromide. Even if the same results be obtained as by *Wijs*' method (which is contested by *Marshall*,[2] *Harvey*,[2] *Archbutt*,[3] *Wesson and Lane*, and especially in the case of tung oil by *Boughton* and by *Kreikenbaum*[4]), it appears to be a superfluous addition to a well-tried process. The author would therefore deprecate the use of *Hanus*' method, as the publication of numbers obtained by this process only serves to encumber unnecessarily the already too bulky literature on this subject.

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[1] *Chem. Revue*, 1899, 1.

[2] Lewkowitsch, *Analyst*, 1899, 259.

[3] A. H. Gill and W. O. Adams, *Journ. Amer. Chem. Soc.*, 1900, 12. Lewkowitsch, *Analyst*, 1900, 33 ; *Jahrbuch der Chemie*, 1898, viii. 395 ; 1902. xii. 366. Wijs, *Analyst*, 1900, 33 ; *Zeits. f. Unters. d. Nahrgs- v. Genussm.*, 1902, 497. A. Marshall, *Journ. Soc. Chem. Ind.*, 1900, 213. F. W. Hunt, *Journ. Soc. Chem. Ind.*, 1902, 454. T. F. Harvey, *Journ. Soc. Chem. Ind.*, 1902, 1437 ; 1904, 414. Foerster, *Zeits. f. angew. Chem.*, 1902, 1207. Tolman and Munson, *Journ. Amer. Chem. Soc.*, 1903, 244 ; 1904, 826. L. Teychené, *Journ. Pharm. Chim.*, 1903 (6), 371. Mascarelli and Blasi, *Gazz. chim. ital.*, 1907 (37), i. 113. A. Leys, *Bull. Soc. Chim.*, 1907, 1, 633. D. A. Bartlett and Sherman, *School of Mines Quarterly*, 1909 (31), 55.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901, 913. Cp. also, C. A. Jungclaussen,

It has been repeatedly stated that the subdivisions adopted in this work for the large classes of vegetable and animal oils, fats, and waxes are based on the magnitude of the iodine values. The following table enumerates most known oils, fats, and waxes. (For less important oils, fats, and waxes Vol. II. of this work should be consulted.) The subdivisions are arranged according to the magnitude of the iodine values, subject, however, to the grouping together of the members of some naturally related oils and fats, such as the oils belonging to the rape oil group, the oils obtained from the fruits of the plants belonging to the *Rosaceæ*, *Myristicaceæ*, and others.

The numbers given are mean values, collated from the best observations. The individual observations are given under the heading of each oil, fat, or wax in Vol. II. Chapter XIV. In some cases I have thought it preferable to give the most reliable values instead of the mean values.

It will be seen that the oils, fats, and waxes arrange themselves in a natural order, beginning with oils, fats, and waxes of the highest iodine value, and passing, through slight gradations, to oils, fats, and waxes having the lowest iodine absorption.

Chem. Centr., 1901, ii. 1324 ; L. M. Tolman and L. S. Munson, *Journ. Amer. Chem. Soc.*, 1903 (25), 244 ; L. E. Levi and E. V. Manuel, *Journ. Amer. Leather Chem. Assoc.*, 1908, 386.

[1] *Annal. chim. analyt. appl.*, 1900 (5), 128.

[2] A. Marshall, *Journ. Soc. Chem. Ind.*, 1900, 213. T. F. Harvey, *Journ. Soc. Chem. Ind.*, 1902, 1437 ; 1904. 414.

[3] *Journ. Soc. Chem. Ind.*, 1904, 306.

[4] *Journ. Ind. and Eng. Chem.*, 1910, 205.

[TABLE

Iodine Values of Oils, Fats, and Waxes

Oil.	Class.	Group.	Iodine value.
Perilla	Drying oils		196-206·1
Linseed			173-201
N'Gart			177·3-204
Tung Chinese			170·6
Japanese			152·9
Lallemantia			162·1
Candle nut			163·7
Stillingia			160·6
White acacia			161·0
Cedar nut			159·2
Garden rocket			155·1
Hemp seed			148
Buckthorn			155
Burdock			153·6
Gynocardia			152·4
Walnut, Nut			145
Arbutus unedo			147·8
Linaria			140·0
Munketti			135-147
Safflower			129·8-149·9
Kaya			133·4-138
Inukaya			130·3
Echinops			138·1-141·2
Soya bean			137-143
Poppy seed			133-143
Asparagus seed			138
Amoora			134·9
Manihot			137·0
Melia azedarach			135·6
Croton Elliotianus			138·5
Henbane			138 ; 131
Millet seed			130·4
Niger seed			126·6-133·8
Sunflower			119-135
Yellow acacia			128·9
Para rubber tree seed			128·3
Service berry			128·5
Celosia			126·3
Argemone			121·2
Fir seed			119·5
Pine nut			101·3
Madia			118·5
Strawberry seed			180·3
Raspberry seed			174·8
Hawthorn seed			152·8
Currant seed			152·5
Blackberry seed			147·8
Mulberry seed			141·5
Indian laurel			118·6
Tobacco seed			118·6
Cameline	Semi-drying oils	Cotton seed oil group	135-142
Grape seed			96 ; 143
Daphne			126·1
Clover, red			124·3
,, white			119·7
Pumpkin seed			123-130
Water melon			118

Iodine Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Iodine Value.
Melon seed	Semi-drying oils	Cotton seed oil group	101·5
Maize (corn)			111-130
Tomato seed			117·8
Persimmon seed			116·8
Wheat			115·4
Datura			113
Beech nut			104-111
Kapok			116
Cotton seed			108-110
Sesamé			103-108
,, first expression			106-114
Basswood			111·0
Lemon pips			109·2
Luffa seed			108·51
Myrtle seed			107·5
Ikpan seed			106·0
Anis seed			105·3
Croton			102-104
Zachun			105·0
Curcas, purging nut			98-110
Brazil nut			106·2
Mucuna			103·95
Sorghum			98·9
Coumou			80
Pinot			136 (?)
Garden cress		Rape oil group	109-139
Ravison			101-122
Hedge mustard			105
Rape (colza)			94-102
Black mustard			96-110
White mustard			92-97
Radish seed			93-96
Jamba			95·4
Small fennel	Non-drying oils		116·2
Quince			113·0
Cherry kernel			110-114
Cherry laurel			108·9
Apricot kernel			96-108
Plum kernel			93·3-100·3
Peach kernel			93-109
Almond			93-97
Wheat meal			96·1-112·5
Sanguinella			100·8
Acorn			100·7
Californian nutmeg			94·7
Owala			98·4
Arachis			83-100
Rice			91·7-106·5
Tea seed			88
Tsubaki			80·6
Sasanqua			82·0
Njore-Njole			93·4

Iodine Values of Oils, Fats, and Waxes—continued

Oil.	Class.	Group.	Iodine Value.
Inoy kernel	Non-drying oils		89·75
Pistachio			87·3-92·5
Hazel nut			83-90
Koéme			88-100
Elderberry			81·44-110
Elozy			85·1
Staff tree			86·7
Olive			79-88
Olive kernel			87·4
Calophyllum			92·8
Oleander			88
Coffee berry			85-87
Birch seed			83·6
Ungnadia			82·0
Ben			88-100
Strophanthus			73·02-101·6
Senega root			81·8
Lycopodium			81
Tropæolum			73·7
Paradise nut			71·64
Secale			71·0-74·6
Canari			65·1
Castor		Castor oil group	83-90
Menhaden	Marine animal oils	Fish oils	139-173
Japanese sardine			121-187
Sardine			161-193
Salmon			161·42
Herring			123·5-142
Stickleback			162·0
Sturgeon			125·3
Cramp fish			107·3
Sunfish			102·7
Cod liver		Liver oils	154·5-181·3
,, ,, mean			167
Haddock liver			154·2
Skate liver			157·3
Tunny fish			155·9
Shark liver			114·6
Coal fish liver			137-162
Ling liver			132·6
Seal		Blubber oils	127-193
Whale			121-146·6
Turtle			112
Dugong			66·6
Dolphin body			99·5-126·9
Dolphin jaw			32·8

Iodine Values of Oils, Fats, and Waxes—continued

Oil or Fat.	Class.	Group.	Iodine Value.
Porpoise body	Marine animal oils	Blubber oils	88-119
Porpoise jaw			22-50
Brown fish			111·2
Chrysalis	Terrestrial animal oils		116-132
Egg			68·5-81·6
Sheep's foot			74·2
Horses' foot			73·8-90
Neat's foot			69·3-76
Chaulmoogra	Vegetable fats	Chaulmoogra oil group	90·7-104
Hydnocarpus			101·9
Lukrabo			82·5-86·4
Parkia		Laurel oil group	91·6
Pongam			89·4-94·0
Laurel			68-96
Carapa			65-72·1
Nux vomica			69·4-79·3
Baobab			54-78
Margosa			69·6
Niam			68·4
Kadam seed			66-68·9
Inukusu			66·08
Mowrah seed			53-68
Illipé butter			50·1
Champaca			60-25
Njave			56
Aouara		Palm oil group	75·3
Palm			51·5-57
Gamboge butter			53·7-55·5
Akee			49·1
Macassar			48-55
Sawarri			49·5
Mafura tallow			45·5
Phulwara butter			42·1
Nutmeg butter		Myristica group	36-58
Ucuhuba			9·5
Ochoco			1·72
Shea butter		Cacao butter group	54-67
Surin			42·3
Mkányi			41·9
Rambutan tallow			39·4
Malabar tallow			38·2
Cacao butter			32-41
Vegetable tallow			19-38·3
Kokum butter			25-34
Borneo tallow			30

Iodine Values of Oils, Fats, and Waxes—continued

Oil or Fat.	Class.	Group.	Iodine Value.
Muriti	Vegetable fats	Cocoa nut oil group	25·2
Mocaya			24·63
Cohune			13·2
Areca nut			12·5
Maripa			9·5-17·4
Aouara kernel			10·8
Palm nut			13-17
Cocoa nut			8-10
Cocos acrocomoides			4·8
Dika		Dika fat group	5·2
Tangkallak			2·28
Cáy-Cáy			6·7
Kusu			4·5
Japan wax			4·9-15·1
Myrtle wax			2·9
Icebear	Animal fats	Drying fats	147
Rattlesnake			105·6
Blackcock		Semi-drying fats	121·1
Lynx			110·6
Marmot			109·1
Hare			102·2
Rabbit (wild)			99·8
Horse			71-86
Wild duck			84·6
Rabbit (tame)		Non-drying fats	67·6
Horse marrow			79·1
Goose (domestic)			59-71
Goose (wild)			99·6
Chicken			66·7
Polecat			62·8
Human, adult			57-67
Domestic duck			58·5
Lard			46-70
Fat from wild boar			76·6-85
Dog			58·5
Wild cat			57·8
Domestic cat			54·5
Beef marrow			55·4
Bone			45-55·8
Beef tallow			38-46
Mutton tallow			35-46
Elk			35·0
Reindeer			31·4-35·8
Roebuck			32·1
Fallow buck			26·4
Stag			20·5-25·7
Butter		Milk fats	26-50

Iodine Values of Oils, Fats, and Waxes—continued

Waxes.	Class.	Group.	Iodine Value.
Sperm oil	Liquid waxes		81-90
Arctic sperm oil			67-89
Carnaüba wax	Solid waxes	Vegetable waxes	13·5
Flax wax			9·6
Wool wax		Animal waxes	17·1-28·9
Beeswax			7·9-11
Rump gland wax			15·5-26·5
Spermaceti			3·8
Insect wax			1·4

The determination of the iodine value furnishes one of the most valuable characteristics in technical fat analysis. If we have to identify a natural oil, fat, or wax, the iodine value indicates in an unmistakable manner the class to which it may belong. The iodine value will thus, as a rule, lead in the quickest manner to the identification of a given natural oil, fat, or wax. Furthermore, if a hitherto unknown specimen be under examination, the iodine value will at once point to the most likely class or group in which the new natural oil or fat should be placed in the system.

This characteristic is all the more valuable as the age of an oil does not materially affect the iodine absorption, provided the oil has not undergone any important change, such as oxidation. Changes due to oxidation are prominently noticeable in the case of drying, fish, and liver oils; less so in the case of semi-drying and blubber oils. The influence of exposure to *light* and *air* on the iodine values of some oils has been examined by many observers. In the following table the data given by *Ballantyne* [1] are reproduced :—

Kind of Oil.	Original Iodine Value.	After Six Months' Exposure to Sunlight.	
		Protected against Access of Air.	Exposed to Air.
Linseed oil	173·46	172·88	166·17
Cotton seed oil	106·84	106·40	100·12
Rape oil	105·59	105·27	102·13
Arachis oil	98·67	97·60	93·20
Castor oil	83·63	83·27 (after 2 months)	83·27
Olive oil	83·16	82·64	78·24

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[1] *Journ. Soc. Chem. Ind.*, 1891, 31 ; cp. Richter, *Zeits. f. angew. Chem.*, 1907, 1605 ; cp. also footnote, p. 397.

The influence of " blowing " with air on the iodine value of oils and fats will be gathered by comparing the numbers given under the headings of the individual oils, fats, and waxes in Vol. II. Chap. XIV., with those recorded in the section " Oxidised Oils " in Vol. III. Chap. XV. It need therefore be only stated in general terms that a considerable diminution of the iodine absorption power is produced by " blowing " or oxidising.

The influence of the unsaponifiable matter in the oils and fats on the iodine value is, in those cases, where the amount of unsaponifiable is very small, negligible ; in those cases, however, where the unsaponifiable matter has a high iodine value (*e.g.* in laurel oil) the iodine value of the total fatty acids, freed from unsaponifiable matter, will be appreciably lower than that of the oil or fat.

Molinari[1] and his collaborators have shown that glycerides of unsaturated fatty acids—as also cholesterol and phytosterol—absorb as many molecules of *ozone* as they contain pairs of doubly linked carbon atoms ; hence the amount of ozone absorbed by unsaturated fatty substances should correspond exactly to the iodine values. For the description and criticism of this method see Chapter VII. p. 467.

3. Reichert (Reichert-Meissl, Reichert-Wollny) Value

The Reichert (or Reichert-Meissl) value indicates the number of cubic centimetres of decinormal potash requisite for the neutralisation of that portion of the soluble volatile fatty acids which is obtained from 2·5 (*or* 5) *grms. of a fat or wax by the Reichert distillation process.*

From the table containing the saponification values of pure triglycerides (p. 383), it will be gathered that the lower the molecular weight of a triglyceride, the higher is its saponification value. Hence, oils and fats containing notable proportions of glycerides of volatile fatty acids are characterised by saponification values exceeding 200.

The occurrence of volatile fatty acids in natural oils and fats was first observed by *Chevreul*, who was also the first to separate them from other fatty acids by distillation. Yet even at present there is no convenient method at our disposal to determine quantitatively the total content of volatile fatty acids in an oil or fat. *Angell and Hehner*[2] endeavoured to determine the amount of the volatile acids of butter fat by distillation, but as they did not obtain concordant results (as widely divergent results as 4·79 and 7·48 per cent were found by them) the method was abandoned. *Lechartier*[3] tried to separate the volatile acids of butter fat from the non-volatile acids by saponifying butter fat with sodium hydrate, adding tartaric acid, and distilling off the volatile acids. The distillate was neutralised with baryta and the barium salts weighed. *Lechartier* ascertained that from 50 grams of butter fat, 6 grams of barium salts were obtained, whilst tallow yielded but one-twentieth of this quantity. The practical application of this correct principle met, however, with insuperable difficulties, owing to the impossibility of distilling off the total amount of volatile acids without decomposing them to some extent.

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[1] Molinari and Fenaroli, *Berichte*, 1908, 2793.

[2] *Butter: Its Analysis and Adulteration*, London, 1874.

[3] *Annales agronomiques*, 1875, 456.

Reichert showed, however, that by determining a *definite* proportion of the volatile soluble acids obtained under certain fixed conditions, reliable indications could be arrived at in the examination of butter fat. Although *Reichert's*[1] process does not yield absolute numbers, still it constitutes a valuable method in that it furnishes a *measure* of the total volatile acids present in an oil, fat, or wax. For purposes of comparison, notably in the examination of butter fat, the relative numbers thus obtained are of great importance in fat analysis.

Reichert originally proposed to ascertain the number of c.c. of decinormal alkali required for the saturation of the soluble volatile fatty acids obtained from 2·5 grms. of substance; at present it is customary to take 5 grms. as first suggested by *Meissl*. In order to avoid errors, the weight of fat to which the value relates should always be stated. In the following pages the *Reichert* (R.) value always refers to 2·5 grms. of substance and the *Reichert-Meissl* (R.M.) value, or *Reichert-Wollny* (R.W.) value, to 5 grms.[2] As the *Reichert* value is an arbitrary one, it is absolutely essential to adhere strictly to the following details:—

Weigh off accurately 5 grms.[3] of the melted and purified fat in a flask of about 200 c.c. capacity, and add about 2 grms. of stick potash (conveniently kept in stock in pieces of about the same length) and 50 c.c. of 70 per cent alcohol. Saponify by heating on the water-bath with frequent shaking, until the alcohol has evaporated off completely. Dissolve the remaining soap paste in 100 c.c of water, add 40 c.c. of dilute sulphuric acid (1 : 10) and a few small pieces of pumice. Fit to the flask a T-piece provided with a bulb, and connect with a *Liebig* condenser. Distil the liquid carefully so that 110 c.c. pass over within about one hour. The distillate is received in a measuring flask, and 100 c.c. are filtered into another measuring flask. Add phenolphthalein to the filtered liquid, and titrate with decinormal caustic potash until the acid is exactly neutralised. The number of c.c. used is multiplied by 1·1 and thus the *Reichert-Meissl* value is obtained. This value is about equal to the *Reichert* value multiplied by 2·2 (cp. Vol. II. Chap. XIV. "Butter Fat").

Thus, if 28 c.c. of decinormal caustic alkali are obtained for 5 grms. of butter fat, the *Reichert-Meissl* value of that butter fat is 28.

The necessity of using alcohol free from acid and aldehyde must be emphasised. The safest plan is to carry out a blank test side by side with the sample, and to take the difference between the two determinations as the actual result. Even the purest alcohol will give a small amount of volatile acid in the blank test. Impure alcohol gives rise to the formation of acetic acid, and must therefore be rejected altogether.

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[1] *Zeits. f. analyt. Chem.*, 1879, 18, 68.

[2] It should be distinctly noted that the *Reichert-Meissl* value is not necessarily twice the *Reichert* value.

[3] *Dingl. Polyt. Journ.*, 233, 229.

It should be distinctly understood that only a portion of the volatile fatty acids is recovered by this distillation process. *Richard Meyer* showed that on distilling in a current of steam a value greater by 25 per cent is obtained. *H. D. Richmond*[1] stated, that in the case of butters only about 87 per cent of the total volatile acids are found in the distillate obtained by the *Reichert-Wollny* process. The author ascertained that 2·5 grams of butter fat distilled in a current of steam until 500 c.c. were collected, required 22 c.c. of decinormal potash. *Jensen*[2] stated that in the case of butter fat, the distillate obtained by the *Reichert-Meissl* process contains 85 to 88 per cent of the total butyric acid, 85 to 100 per cent of the total caproic, and 24 to 25 per cent of the total caprylic acid of the fat (cp. Chap. VIII.). Hence the necessity of always working under strictly the same conditions becomes apparent.[3]

Traces of higher fatty acids[4] pass over together with the volatile acids, and are found in the distillate as minute oily drops or solid particles. They do not, however, vitiate the result, as they are removed by subsequent filtration. (Cp. Chap. VIII. and "Butter Fat," Vol. II. Chap. XIV.)

The excellent *Reichert* process has not escaped the fate of nearly all modern methods used in fat analysis, viz. that of receiving at the hands of numerous analysts a number of supposed improvements, most of which are altogether insignificant or, at best, offer doubtful advantages.

Wollny[5] raised a number of objections to the foregoing process, pointing out the following sources of error: (1) absorption of carbon dioxide during saponification, introducing an error up to 10 per cent; (2) formation of esters during the saponification, causing a loss of 8 per cent; (3) formation of esters during the distillation with a loss of 5 per cent; (4) coherence of the fatty acids during the distillation, which may, in some cases, involve a loss of as much as 30 per cent; (5) the varying form and size of the distillation flask and the time the distillation lasts, which may influence the result to the extent of ± 5 per cent. These objections have been refuted by *v. Raumer and Sendtner*. However, since *Wollny's* process has been adopted by a Joint Committee of the Government Laboratory and the Society of Public Analysts as the standard method for the determination of the soluble volatile fatty acids in butter and margarine, I describe it in the form published by the Committee,[1] and add some explanations in brackets.

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[1] *Analyst*, 1895, 218.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, 272.

[3] The French official method (prescribed for the examination of butter fat) aims at the determination of the total amount of soluble fatty acids. Cp. Chap. VIII.

[4] It has been stated that traces of sulphur also occur in the distillates from butter fat. As sulphur is found even if phosphoric acid be substituted for sulphuric acid, it would appear that sulphur in the distillate must be ascribed to traces of sulphurised compounds in butter fat, or at least in some butter fats. Cp. A. Brüning, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 667.

[5] *Journ. Soc. Chem. Ind.*, 1887, 831.

Reichert-Wollny Process.—Five grams of liquefied fat are introduced into a 300 c.c. flask, of the form shown in Fig. 37 (length of neck 7 to 8 centimetres, width of neck 2 centimetres). Two c.c. of a caustic soda solution, prepared by dissolving 98 per cent sodium hydrate in an equal weight of water—protected from the action of atmospheric carbonic acid—and 10 c.c. of (about 92 per cent) alcohol are added, and the mixture is heated for fifteen minutes under a reflux condenser, connected with the flask by a T-piece, in a bath containing boiling water. The alcohol is evaporated off by heating the flask on the water-bath for about half an hour, or until the soap is dry. One hundred c.c. of hot water which have been kept boiling for at least ten minutes (to drive out all dissolved carbonic acid, the retention of which would vitiate the result) are added, and the flask is heated until the soap is dissolved. Forty c.c. of normal sulphuric acid and three or four fragments of pumice or broken pipe-stems are added, and the flask is at once connected with a condenser by means of a glass tube 7 millimetres wide, and 15 centimetres from the top of the cork to the bend. At a distance of 5 centimetres above the cork is a bulb 5 centimetres in diameter. The flask is supported on a circular piece of asbestos 12 centimetres in diameter, having a hole in the centre, 5 centimetres in diameter, and is first heated by a very small flame, to

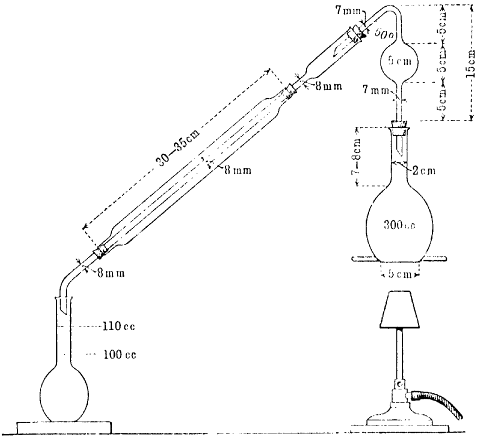

Fig. 37.

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[1] *Analyst*, 1900, 309.

fuse the insoluble fatty acids, but the heat must not be so great as to cause the liquid to boil; when fusion is complete, the heat is increased,[1] 110 c.c. are distilled off into a graduated flask, the distillation lasting about 30 minutes (from 28 to 32 minutes). The distillate is shaken, 100 c.c. are filtered into a flask, 0·5 c.c. of phenolphthalein solution (1 grm. in 100 c.c. alcohol) is added, and the filtrate titrated with decinormal soda or baryta solution. In precisely the same manner (with the same reagents), a blank test should be made, and the amount of decinormal alkali required to neutralise the distillate ascertained. This should not exceed 0·3 c.c. The volume of decinormal solution of alkali used, less the figure obtained in the blank experiment, is multiplied by 1·1. The number so found is the *Reichert-Wollny* value.

The well-known fact (see above) that in the *Reichert* distillation process only part of the volatile acids is distilled off has induced some analysts to modify it and to attempt to obtain the total quantity. Thus it has been proposed to repeat the distillation several times with fresh quantities of water. But not only does this take up more time than can be conveniently allowed for a technical analysis, but a source of error is thereby introduced, inasmuch as with each distillation decomposition of the non-volatile acids takes place. (Cp. also Chap. VIII.)

In order to obviate the (supposed, cp. Chap. II.) formation of ethylic esters of the volatile fatty acids (*Wollny's* second objection), *Leffmann and Beam*[2] (cp. Vol. II. Chap. XIV.) proposed to saponify with a concentrated solution of caustic soda in glycerin. This process is convenient owing to its rapidity (see "Butter Fat," Vol. II. Chap. XIV.), and has therefore been introduced by *Polenske* in the process of determining the titration number of the insoluble volatile acids (see below). The method is carried out as follows: 5 grms. of butter fat are placed in a 300 c.c. flask and heated with 20 c.c. of a solution of caustic soda in glycerin (prepared by dissolving 100 grms. of caustic soda in an equal weight of water and mixing 20 c.c. of this solution with 180 c.c. of pure concentrated glycerin) over a naked flame for 2 to 3 minutes, until the water has evaporated off and the liquid has become clear (cp. also Vol. II. Chap. XIV. "Butter Fat").

Wrampelmeyer (*Landw. Versuchsstat.*, 1897 (49), 215) states that caustic potash does not yield satisfactory results. It is difficult to understand why this should be so; hence *Wrampelmeyer's* statement requires confirmation. Caustic potash, in fact, ought to work better, as it would yield more readily soluble soaps.[3]

Paal and Amberger[4] state that in the case of cocoa nut oil and butter fats containing considerable proportions of cocoa nut oil, the saponification with alcoholic potash proceeds more rapidly than with glycerol soda or glycerol potash.

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[1] The heating of the asbestos plate itself should be guarded against, as serious errors arise if the asbestos should become overheated.

[2] *Analyst*, 1891, 153; cp. also Karsch, *Chem. Zeit.*, 1896, 207.

[3] Cp. also Siegfeld, *Chem. Zeit.*, 1908, 1128.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, 10.

The values obtained by *Leffmann and Beam's* method are practically identical with those obtained by the *Reichert-Wollny* process, as the author can testify from his own experience.

Instead of saponifying with alcoholic caustic alkali, *Kreis* proposed, in the case of butter fat, to saponify with concentrated sulphuric acid. This method cannot be recommended. The details and a criticism of the method are given in Vol. II. Chap. XIV. under the heading "Butter Fat."

Whilst in the case of butter fat it is admissible to work with 2·5 grms.,[1] as was proposed originally by *Reichert*, and to multiply the result by 2·2, in order to obtain numbers comparable with those found by the *Reichert-Meissl* or *Reichert-Wollny* process, deviations from the figures 2·5 grms. and 5 grms. would produce misleading results, as the following table, due to *Arnold*,[2] shows :—

Volatile Fatty Acids in Butter Fat determined by the Reichert-Meissl Process

Weight of Butter Fat.	c.c. $\frac{1}{10}$ normal KOH required for Soluble Volatile Acids.
1 grm.	6·55
2 grms.	12·05
3 ,,	17·38
4 ,,	22·28
5 ,,	27·60
10 ,,	50·44

When using 10 grms. of butter fat in the *Reichert-Meissl* process, *Paal and Amberger* found in one case a considerably lower *Reichert-Meissl* value than under normal conditions ; in other cases the *Reichert-Meissl* values obtained with 10 grms. approximated to those obtained under normal conditions.

The quantity of 5 grms. must, however, be rigorously adhered to in the case of cocoa nut oil and palm kernel oil. For whereas in the case of butter fat the large proportion of butyric acid in the volatile acids renders the result less dependent on the amount of substance weighed off, the absence of butyric acid in cocoa nut oil and palm nut oil and the presence of large quantities of caproic and caprylic acids lead to completely different results when varying quantities of substance are used. This becomes apparent by a glance at the following table, due to *Orla Jensen* :[3]—

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, 10.

[2] *Ibid.*, 1907, xiv. 162.

[3] *Ibid.*, 1905, 272.

Volatile Fatty Acids in Cocoa Nut Oil determined by the Reichert-Meissl Process

Weight of Cocoa Nut Oil.	c.c. $\frac{1}{10}$ norm. KOH for Soluble Volatile Acids.
1·0654, say 1 grm.	19·2
1·8126 „ 2 grms.	13·0
3·9726 „ 4 „	7·7
4·9907 „ 5 „	6·8
6·3932 „ 6 „	6·0
7·8643 „ 8 „	5·5
11·9168 „ 12 „	4·8

This point becomes all the more accentuated by comparing the results recorded in the preceding table with those ascertained by *Arnold*.[1]

Weight of Cocoa Nut Oil.	c.c. $\frac{1}{10}$ norm. KOH for Soluble Volatile Acids.
1 grm.	4·68
2 grms.	6·38
3 „	7·04
4 „	7·87
5 „	9·35
10 „	10·45

In the case of " Apeiba oil " the author's experiments show that the difference is not so pronounced, as in the case of cocoa nut and palm nut oils. Whereas the volatile soluble acids from 3·1 grms. of Apeiba oil required 7·57 c.c. $\frac{1}{10}$ norm. KOH, 5·3 grms. required 7·75 c.c.

Since the volatile fatty acids of butter fat are for the most part also soluble in water (see above), several methods were proposed for the determination of the *soluble* acids (see Chap. VIII.).

Most of the naturally occurring oils and fats contain but small quantities of volatile soluble fatty acids. Therefore, the *Reichert* values of the majority of oils, fats, and waxes are very low. As a rule they are below 0·5 ; hence, the *Reichert-Meissl* values of the majority of oils, fats, and waxes are below 1·0. It is evident, therefore, that a somewhat high *Reichert-Meissl* value will constitute a distinctive characteristic of an oil, fat, or wax, and that very valuable indications as to the nature of an oil, fat, or wax are obtained by determining its soluble volatile acids by the *Reichert-Meissl* process.

In the following table I collate those oils, fats, and waxes for which the *Reichert-Meissl* numbers exceeding 1·0 have been recorded. It must, however, be borne in mind that many of the oils enumerated in the following table would disappear from it, if the specimens had been examined in the fresh state. These doubtful oils have been marked with an asterisk.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 165.

Reichert (R.) and Reichert-Meissl (R.M.) Values

* Lallemantia oil	1·55 (R.)
* White acacia oil	1·2 (R.M.)
* Cedar nut oil	2·0 (R.M.)
* Yellow acacia oil	2·7 (R.M.)
* Strawberry seed oil	2·1 (R.M.)
* Clover oil, red ; white	3·3 ; 3·5 (R.M.)
Sorindeia oil	7·92 (R.) ?
* Maize (corn) oil	4·2-9·9 (R.)
* Kapok oil	3·3 (R.)
Myrtle seed oil	9·65 (R.M.)
Croton oil	12-13·6 (R.M.)
* Sorghum oil	2·1 (R.M.)
Spindle tree oil	35·31 (R.M.)
* Small fennel oil	5·4 (R.M.)
* Wheatmeal oil	2·8-4·95 (R.M.)
Oleander oil	10·26 (R.M.)
Senega root oil	6·43 (R.M.)
Lycopodium oil	7·3 (R.M.)
Apeiba oil	7·75 (R.M.)
Malukang oil	45·55 (R.M.)
Turtle oil	4·6 (R.M.)
Dugong oil	2·5 (R.)
Dolphin oil	5·6 (R.)
Dolphin jaw oil	65·92 (R.)
Porpoise body oil	23·5-40·7 (R.)
Porpoise jaw oil	47·77-65·8 (R.)
Brown fish oil	42·1 (R.M.)
* Chrysalis oil	3·38 (R.M.)
* Laurel oil	1·6-5·4 (R.)
* Carapa oil	3·5 (R.M.)
* Inukusu oil	2·05 (R.M.)
Macassar oil	9 (R.M.)
* Nutmeg butter	1-2·1 (R.M.)
Muriti fat	5·0 (R.M.)
Mocaya oil	7·0 (R.M.)
Areca nut fat	4·2 (R.M.)
Maripa oil	4·45 (R.M.)
Palm kernel oil	5·6 (R.M.)
Cocoa nut oil	7 (R.M.)
Tonka butter	5·4 (R.M.)
Butter fat	26-33 (R.M.)
* Flax wax	9·27 (R.M.) ?

The extraordinarily high numbers of porpoise and dolphin oils are due to the presence of valeric (?) acid. Amongst the solid fats, butter fat is notable on account of its high *Reichert-Meissl* value ; therefore this number affords a most valuable means of identifying butter fat and distinguishing it readily from other fats.

4. Titration Number of Insoluble Volatile Fatty Acids

The titration number of insoluble fatty acids indicates the number of c.c. of decinormal potassium hydrate required for the neutralisation of that portion of the insoluble volatile fatty acid which is obtained from 5 grms. of fat or wax by the Polenske process.

In the description of the *Reichert* distillation process it has been pointed out that the distillate of 110 c.c. must be filtered in order to remove those insoluble volatile fatty acids which have been carried over with the steam and have condensed to liquid or solid acids. These are removed when filtering the distillate in order to obtain the 100 c.c. which are titrated for the determination of the *Reichert-Meissl* value.

Salkowski [1] was the first to propose the determination of the insoluble volatile fatty acids by dissolving the residue, left on the filter in *Reichert's* distillation process, in alcohol and titrating with decinormal alkali. *Salkowski* distilled first in the manner directed by *Reichert*, and then drove off further quantities of both soluble and insoluble fatty acids by filling up the flask several times in succession with 110 c.c. of water. The details of two experiments, in each of which 5·945 grms. of cocoa nut oil were used, may be given here.

	c.c. of decinormal Alkali required for Soluble Volatile Acids in 100 c.c.	c.c. of decinormal Alkali required for Insoluble Volatile Acids in total Distillate of 100 c.c.
I. 1st distillate .	7·00	10·90
2nd distillate .	3·20	7·75
	10·20	18·65
II. 1st distillate .	6·70	10·90
2nd distillate .	3·45	7·25
3rd distillate .	2·55	6·35
4th distillate .	1·80	6·00
5th distillate .	1·50	5·20
	16·00	35·70

As this method is too cumbersome, special methods, simulating the *Reichert* process and based on the principle introduced by *Salkowski*, have been worked out in recent years independently by *Müntz and Coudon* and by *Polenske*. Since *Müntz and Coudon's* process applies especially to the French official method of examining butter fat, and has therefore not acquired that general application which *Polenske's* process has gained, the former process will be described under "Butter Fat," Vol. II. Chap. XIV.

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[1] *Zeits. f. analyt. Chem.*, 1887, xxvi. 581.

Polenske[1] adapts himself so closely to the *Reichert-Meissl* process, that both determinations, viz. that of the *Reichert-Meissl* value and of the titration number of the insoluble volatile acids, can be carried out consecutively in one operation.

Polenske saponifies 5 grms. of filtered fat (butter fat), by the *Leffmann-Beam* process, with 20 grms. of glycerin and 2 c.c. of caustic soda solution (prepared from equal parts of sodium hydrate and water) in a 300 c.c. flask by heating over a free flame. The solution is allowed to cool below 100° C., 90 c.c. of water are added, and the mass dissolved by warming on the water-bath to about 50° C. The solution must be clear and almost colourless. In case a brown solution be obtained, the test must be rejected. 50 c.c. of dilute sulphuric acid (containing 25 c.c. of pure concentrated sulphuric acid in 1000 c.c.) and some *powdered* pumice (not aluminium wire) are added to the hot soap solution; the flask is then immediately attached to the condenser. The apparatus to be employed must correspond in all details to the dimensions given in Fig. 38. An asbestos plate must be used exactly as described in connection with Fig. 37; on no account must wire gauze be used for heating, as very capricious results are obtained owing to the irregular heating. The heat must be so regulated[2] that within nineteen to twenty minutes 110 c.c. are distilled off;[3] the cooling water must be supplied at such a rate that the distillate does not drop into the 110 c.c. flask at a higher temperature than 20°-23° C. As soon as 110 c.c. have distilled over, the distillation is interrupted, the flask is removed, and is replaced by a 20 c.c. measuring cylinder.

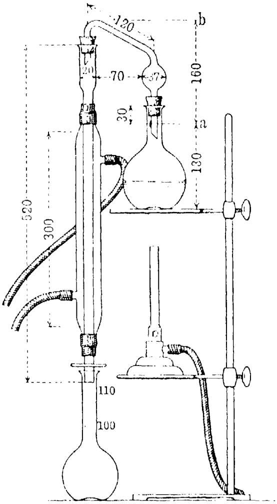

Fig. 38.

The distillate, which must not be shaken through, is immersed almost completely in water of 15° C. After about five minutes the neck of the flask is slightly tapped, so that the oily drops floating on the surface may adhere to the walls of the flask. After a further ten minutes the consistence of the insoluble acids is noted, with a view to ascertaining whether they form a solid (semi-solid) mass or oily drops. The contents of the flask are then mixed by turning the corked flask four or five times upside down, avoiding, however, violent shaking. 100 c.c. are filtered off through a filter of 8 cm. diameter, and titrated with decinormal caustic potash, as is done in the determination of the *Reichert-Meissl* value. In order to remove the soluble acids completely, the insoluble volatile acids on the filter are washed three times in succession with 15 c.c. of water, which have been passed severally through the tube of the condenser, the 20 c.c. measuring cylinder, and the 110 c.c. flask. These wash-waters are thrown away. In order to collect the insoluble volatile acids adhering to the tube of the condenser, the measuring cylinder, and the 110 c.c. flask, these vessels are rinsed three times in succession with 15 c.c. of neutralised 90 per cent alcohol, and the alcoholic washes poured through the filter, each quantity being allowed to drain before a fresh wash is poured on the filter. The alcoholic filtrate is then titrated with decinormal alkali.

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[1] *Arbeit. aus dem kaiserl. Gesundheitsamte*, 1904, 545.

[2] With regard to a proposal to regulate the temperature of the still-head cp. C. Revis and E. R. Bolton, *Analyst*, 1911, 334. This, as also the adoption of a modified Polenske apparatus proposed by Goske, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912 (xxiv.), 257, would only lead to confusion.

[3] E. R. Bolton, H. D. Richmond, and C. Revis (*Analyst*, 1912, 185) state that if the small hole in the side of the still-head tube (which is to prevent the collection of condensed liquid in the still-head) is much more than 1 cm. from the lower surface of the cork—as originally designed by Polenske—low values are obtained when the proportion of cocoa nut oil in a butter fat is high.

The titration numbers of the insoluble volatile fatty acids of oils and fats having saponification value of about 195, do not exceed 0·5 c.c. or at most 0·65, provided, of course, the specimen be not excessively acid or rancid.

Most characteristic are the titration numbers of the insoluble volatile fatty acids in the case of butter fat, cocoa nut oil, and palm kernel oil, as the following numbers show :—

Oil or Fat.	Titration Number of Insoluble Volatile Fatty Acids. c.c. $\frac{1}{10}$ normal KOH.
Butter fat	2·3-3·3
Cocoa nut oil	15-20
Palm kernel oil	10-12

These numbers are of the greatest importance in the examination of adulterated butter fat, and of margarines for the proportion of cocoa nut oil, palm kernel oil, and milk fat. For the full discussion the reader must be referred to Vol. II. Chap. XIV. "Butter Fat," and Vol. III. Chap. XV. "Edible Fats."

In order to show that it is absolutely necessary to adhere rigorously to the quantity of 5 grms. (especially in the case of cocoa nut and palm kernel oils), the following tables, which are extensions of the tables given p. 422, may be appended :—

Soluble Volatile and Insoluble Volatile Acids of Cocoa Nut Oil
(O. Jensen)

Weight of Cocoa Nut Oil.	c.c. $\frac{1}{10}$ normal KOH required for Soluble Volatile Acids. I.	Insoluble Volatile Acids. II.	Proportion, II : I. III.
1·0654 say 1 grm.	19·2	34·2	1·8
1·8126 ,, 2 grms.	13·0	23·5	1·8
3·9726 ,, 4 ,,	7·7	15·2	1·97
4·9907 ,, 5 ,,	6·8	12·7	1·87
6·3932 ,, 6 ,,	6·0	12·6	2·10
7·8643 ,, 8 ,,	5·5	10·0	1·81
11·9168 ,, 12 ,,	4·8	9·0	1·88

The last columns, added by the author, show that the proportion II : I remains practically the same in the case of cocoa nut oil, whereas in the case of butter fat the proportion I : II increases with the quantity of fat (see Vol. II. "Butter Fat").

Soluble Volatile and Insoluble Volatile Acids of Cocoa Nut Oil
(Arnold)

Weight of Cocoa Nut Oil.	c.c. $\frac{1}{10}$ normal KOH required for Soluble Volatile Acids. I.	Insoluble Volatile Acids. II.	Proportion, II : I. III.
1 grm.	4·68	8·55	1·83
2 grms.	6·38	11·90	1·86
3 ,,	7·04	13·75	1·96
4 ,,	7·87	14·85	1·89
5 ,,	9·35	16·55	1·77
10 ,,	10·45	18·65	1·78

In the case of Apeiba oil no such variation depending on the quantity employed was observed; the author found that for 3·1 grms. of oil 28·82 c.c. and for 5·3 grms 27·08 were required.

In the case of butter fat also the variation in the titration number of the insoluble volatile fatty acids is not so strongly pronounced as in the case of cocoa nut and palm kernel oils. This is shown by the numbers contained in the following table:—

Soluble Volatile and Insoluble Volatile Acids in Butter Fat (Arnold)

Weight of Butter Fat taken.	c.c. $\frac{1}{10}$ normal KOH required for		Proportion, II : I.
	Soluble Volatile Acids. I.	Insoluble Volatile Acids. II.	III.
1 grm.	6·55	1·40	4·67
2 grms.	12·05	1·80	6·70
3 „	17·38	1·90	9·15
4 „	22·28	2·10	10·61
5 „	27·60	2·25	12·27
10 „	50·44	2·70	18·7

Acetyl Value

The acetyl value indicates the number of milligrams of potassium hydrate required for the neutralisation of the acetic acid obtained on saponifying one gram of an acetylated fat or wax.

The determination of the acetyl value (acetyl number) is based on the principle that glycerides containing hydroxylated fatty acids assimilate, on heating with acetic anhydride, one or more acetyl groups, according to whether the fatty acids contain one or more alcoholic hydroxyl groups. The chemical change consists in the replacing of the hydrogen atom of the alcoholic hydroxyl group or groups by the radicle of acetic acid, as explained by the following equations :—

$$\underset{\text{Ricinolein.}}{C_3H_5[O.C_{18}H_{32}O(OH)]_3} + \underset{\text{Acetic anhydride.}}{3(C_2H_3O)_2O} = \underset{\text{Acetyl ricinolein.}}{C_3H_5[O.C_{18}H_{32}O(O.C_2H_3O)]_3} + \underset{\text{Acetic acid.}}{3C_2H_4O_2}$$

$$\underset{\text{Sativin.}}{C_3H_5[O.C_{18}H_{31}O.(OH)_4]_3} + \underset{\text{Acetic anhydride.}}{6(C_2H_3O)_2} = \underset{\text{Tetra-acetyl sativin.}}{C_3H_5[O.C_{18}H_{31}O.(O.C_2H_3O)_4]_3} + 6H_2O.$$

The determination of the acetyl value (first proposed by *Benedikt*, see below) is carried out in the form given to it by *Lewkowitsch* :[1] 10 grms., or any other convenient quantity, are boiled with twice the amount of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser. The solution is then transferred to a beaker of about 1 litre capacity, mixed with 500 to 600 c.c. of boiling water and heated for half an hour, whilst a slow current of carbon dioxide is passed into the liquid through a finely-drawn-out tube reaching nearly to the bottom of the beaker ; this is done to prevent bumping. The mixture is then allowed to separate into two layers, the water is syphoned off, and the oily layer again boiled out in the same manner three successive times. The last trace of acetic acid is thus removed; this is ascertained by testing with litmus paper. Prolonged washing beyond the required limit causes slight dissociation of the acetyl product. This would lead to too low an acetyl value. The acetylated product is then filtered through dry filter-paper in a drying oven to remove water.

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[1] *Journ. Soc. Chem. Ind.*, 1897, 503. This method was adopted at the International Congress of Rome. Cp. *Atti del VI. Congresso internationale di chimica applicata, Rome*, 1907, vol. vii. 488.

The whole operation may be carried out quantitatively, and in that case the fatty matter is washed on the filter with boiling water, until the filtrate no longer reddens sensitive litmus paper. It is advantageous to weigh the fatty matter left on the filter after drying in an oven (cp. Chap. VIII. "Determination of the Insoluble Fatty Acids and Unsaponifiable Matter") if it is desired to ascertain preliminarily, whether in an unknown fat a notable amount of glycerides of hydroxy acids are present (cp. below "Diglycerides and Monoglycerides").

About 5 grms. of the acetylated product are then saponified by boiling with alcoholic potash, as is done in the determination of the "Saponification Value." If the "distillation process" be adopted, it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the "filtration process" be used, the alcoholic potash must be measured exactly. (It is advisable to use in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated off and the soap dissolved in water. From this stage onwards the determination is carried out either by (*a*) the distillation process, or (*b*) the filtration process.

(*a*) *Distillation Process.*—Add dilute sulphuric acid (1 : 10), more than is required to saturate the potash used, and distil the liquid in a current of steam. 600-700 c.c. of water are distilled off. As a rule this will be quite sufficient, for the last 100 c.c. will be found to require no more than 0·1 c.c. of decinormal alkali. Then titrate the distillate with decinormal potash, using phenolphthalein as an indicator, multiply the number of c.c. by 5·61, and divide by the weight of substance taken. This gives the *acetyl value.*

(*b*) *Filtration Process.*—Add to the soap solution a quantity of standardised sulphuric acid, *exactly* corresponding to the amount of alcoholic potash employed, and warm gently, whereupon the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal alkali. The acetyl value is calculated in the manner shown above (*a*).

Both methods give identical results;[1] the latter requires less time and will, therefore, be found more convenient.

The distilled water used in determining the "value" by either the distillation or filtration process must be carefully freed from carbonic acid by previous boiling, as otherwise serious errors will follow. Even the water used for generating steam in the distillation process should be brought into violent ebullition before the steam is passed into the distilling flask. In the case of very hard water this source of error may easily creep in. Check experiments with pure acetic acid will readily guide the operator. In order to facilitate the separation of the insoluble fatty acids in the filtration process, it will be found useful to add a slight excess of mineral acid. Of course this amount, which need not exceed 1 c.c. of normal acid, must be measured accurately and deducted from the alkali required for determining the dissolved acids.[1]

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[1] Freundlich (*Chem. Rev.*, 1908, 106) states that in the case of Njave butter (see Vol. II. Chap. XIV.) divergent results were obtained; the cause of this has not, however, been investigated by him.

Pure triglycerides containing no hydroxylated acids have no acetyl value; pure glycerides of hydroxylated fatty acids yield acetyl numbers which are in complete agreement with theory. In these cases the acetyl value is a *characteristic*. The following table contains the theoretical acetyl numbers of some triglycerides :—

Glyceride	Acetylated Glyceride.				
	Formula.	Molecular Weight.	Saponification Value.	Insoluble[2] Fatty Acids.	Acetyl Value.
			Mgrms. KOH.	Per cent.	Mgrms. KOH.
Ricinolein . .	$C_3H_5[O.C_{18}H_{32}O(O.C_2H_3O)]_3$	1058	318·2	84·49	159·1
Hydroxystearin .	$C_3H_5[O.C_{18}H_{34}O(O.C_2H_3O)]_3$	1064	316·3	84·56	158·1
Dihydroxystearin.	$C_3H_5[O.C_{18}H_{33}O(O.C_2H_3O)_2]_3$	1238	407·8	76·67	271·9
Trihydroxystearin	$C_3H_5[O.C_{18}H_{32}O(O.C_2H_3O)_3]_3$	1412	476·8	70·54	357·6
Sativin . .	$C_3H_5[O.C_{18}H_{31}O(O.C_2H_3O)_4]_3$	1586	530·5	65·81	424·3
Linusin . .	$C_3H_5[O.C_{18}H_{29}O(O.C_2H_3O)_6]_3$	1934	609·2	58·94	522·1

In practical analysis, if a mixture of a pure glyceride of hydroxylated acids of known composition with a pure glyceride which is free from hydroxylated acids be given, the determination of the acetyl value enables us to calculate the proportion of the hydroxylated glyceride.

A case of this kind is exemplified by castor oil, which consists preponderantly of ricinolein. The foregoing table gives 159·1[3] as the acetyl value of pure ricinolein. Suppose the examination of a commercial sample of castor oil gave the acetyl value 150·3; then the percentage of ricinolein in the sample will be found from the proportion 159·1 : 100 : : 150·3 : x ; x = 94·4 per cent.

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[1] Normann (*Chem. Revue*, 1912, 205) proposes an abbreviated method for the determination of the "hydroxyl value." This method cannot be recommended. Cp. also Twitchell's "hydroxyl value," footnote 3, this page. Still more open to very serious criticism are the notes regarding the acetyl value given by Willstätter and Madinaveitia (*Berichte*, 1912, 2828), who claim to have obtained small acetyl values with a specimen of "tristearin." In the author's opinion the two results given by Willstätter and Madinaveitia are due to experimental errors (for a suggested explanation cp. table p. 434.

[2] For the method of determining the insoluble fatty acids see Chap. VIII.

[3] In order to avoid confusion, which seems to have arisen, attention should again be drawn to the definition of the "acetyl value" as given above. (Cp. also *Journ. Soc. Chem. Ind.*, 1897, 504, and *Analyst*, 1899, 321, where it is explained why it is permissible in some cases, namely, when the acetyl value is low, to refer the value to the oil itself, although it is the acetylated product which is weighed off.

Twitchell (*Journ. Amer. Chem. Soc.*, 1907, 566) determines the "hydroxyl value" by esterification of the alcoholic hydroxyl group of fatty acids in the presence of Twitchell's reagent. His "*hydroxyl value*" refers to the oil itself, and although the value is analogous to the "acetyl value," it is not identical with it as, according to the definition given above, the acetyl value refers to the acetylated product.

Free alcohols undergo the same chemical change on heating with acetic anhydride, that is, they also assimilate an acetyl group in exchange for the hydrogen atom in the alcoholic hydroxyl group. This is exemplified by the following equations :—

$$\underset{\substack{\text{Cetyl}\\\text{alcohol.}}}{C_{16}H_{33}OH} + \underset{\substack{\text{Acetic}\\\text{anhydride.}}}{(C_2H_3O)_2O} = \underset{\text{Cetyl acetate.}}{C_{16}H_{33}O.C_2H_3O} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{C_2H_4O_2}.$$

$$\underset{\text{Glycerol.}}{C_3H_5(OH)_3} + \underset{\substack{\text{Acetic}\\\text{anhydride.}}}{3(C_2H_3O)_2O} = \underset{\text{Triacetin.}}{C_3H_5(O.C_2H_3O)_3} + \underset{\substack{\text{Acetic}\\\text{acid.}}}{3C_2H_4O_2}.$$

The following table gives the theoretical acetyl values of a number of pure alcohols :—

Alcohol.	Acetylated Alcohol.		
	Formula of Acetate.	Molecular Weight.	Acetyl Value.
Cetyl alcohol	$C_{16}H_{33}O.C_2H_3O$	284	197·5
Octodecyl alcohol . . .	$C_{18}H_{37}O.C_2H_3O$	312	179·8
Ceryl alcohol	$C_{26}H_{53}O.C_2H_3O$	424	132·3
Melissyl (Myricyl) alcohol .	$C_{30}H_{61}O.C_2H_3O$	480	116·9
Cholesterol Phytosterol	$C_{27}H_{45}O.C_2H_3O$	428	131·1
Glycerol	$C_3H_5O_3(C_2H_3O)_3$	218	772·0

From the acetyl value the proportion of the pure alcohols can be calculated, provided their composition be known. Thus the proportion of glycerol in a commercial glycerin, or of cholesterol in a mixture, can be determined by ascertaining the acetyl value (cp. **Glycerol**, "Acetin Method," p. 448, and "Cholesteryl Acetate," Chapter IX.).

If the chemical composition of a hydroxylated triglyceride contained in an oil or fat, or of an alcohol contained in a wax, be unknown, then the acetyl value would still be a measure of the proportion of hydroxylated triglycerides or of the alcohols respectively. If both hydroxylated triglycerides and alcohols be present simultaneously, the acetyl value would naturally be a measure of the sum of both, viz. hydroxylated triglycerides and alcohols. Even in the latter somewhat more complicated case, the acetyl value would still rank as a *characteristic*, just like the saponification value or the *Reichert-Meissl* value.

The foregoing remarks apply to pure triglycerides and pure waxes, and hold good as long as no other substances capable of assimilating acetyl groups be present. It has, however, been pointed out already that natural oils and fats contain varying quantities of free fatty acids (see below, **Acid Value**), due to the varying amount of hydrolysis which the natural oils and fats have undergone. These partially hydrolysed natural oils and fats contain small quantities of mono- and di-glycerides which are capable of assimilating acetyl groups by exchanging the hydrogen of their alcoholic hydroxyl group or groups for an acetyl group or groups, as is exemplified by the following two equations :—

$$\underset{\text{Monostearin.}}{C_3H_5(OH)_2(O.C_{18}H_{35}O)} + (C_2H_3O)_2O = \underset{\text{Di-acetyl-monostearin.}}{C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{35}O)} + H_2O.$$

$$\underset{\text{Distearin.}}{C_3H_5(OH)(O.C_{18}H_{35}O)_2} + (C_2H_3O)_2O = \underset{\text{Acetyl distearin.}}{C_3H_5(O.C_2H_3O)(O.C_{18}H_{35}O)_2} + C_2H_4O_2.$$

This will be readily seen from the following table, stating the acetyl values of pure mono- and di-glycerides. In the case of those mono- and di-glycerides which contain hydroxylated fatty acids in the molecule, an additional amount of acetic anhydride will be assimilated, thus considerably increasing the acetyl value of such glycerides.

Acetyl Values of Pure Mono- and Di-glycerides

Glyceride of Acid.	ACETYLATED MONOGLYCERIDE.			ACETYLATED DIGLYCERIDE.		
	Formula.	Molecular Weight.	Acetyl Value.	Formula.	Molecular Weight.	Acetyl Value.
Acetic	$C_3H_5(O.C_2H_3O)_2(O.C_2H_3O)$	218	772·0	$C_3H_5(O.C_2H_3O)(O.C_2H_3O)_2$	218	772·0
Butyric	$C_3H_5(O.C_2H_3O)_2(O.C_4H_7O)$	246	684·2	$C_3H_5(O.C_2H_3O)(O.C_4H_7O)_2$	274	614·3
Valeric	$C_3H_5(O.C_2H_3O)_2(O.C_5H_9O)$	260	647·4	$C_3H_5(O.C_2H_3O)(O.C_5H_9O)_2$	302	557·3
Caproic	$C_3H_5(O.C_2H_3O)_2(O.C_6H_{11}O)$	274	614·3	$C_3H_5(O.C_2H_3O)(O.C_6H_{11}O)_2$	330	510·0
Caprylic	$C_3H_5(O.C_2H_3O)_2(O.C_8H_{15}O)$	302	557·3	$C_3H_5(O.C_2H_3O)(O.C_8H_{15}O)_2$	386	436·0
Capric	$C_3H_5(O.C_2H_3O)_2(O.C_{10}H_{19}O)$	330	510·0	$C_3H_5(O.C_2H_3O)(O.C_{10}H_{19}O)_2$	442	380·8
Lauric	$C_3H_5(O.C_2H_3O)_2(O.C_{12}H_{23}O)$	358	470·1	$C_3H_5(O.C_2H_3O)(O.C_{12}H_{23}O)_2$	498	338·0
Myristic	$C_3H_5(O.C_2H_3O)_2(O.C_{14}H_{27}O)$	386	290·7	$C_3H_5(O.C_2H_3O)(O.C_{14}H_{27}O)_2$	554	101·3
Palmitic	$C_3H_5(O.C_2H_3O)_2(O.C_{16}H_{31}O)$	414	271·0	$C_3H_5(O.C_2H_3O)(O.C_{16}H_{31}O)_2$	610	91·99
Stearic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{35}O)$	442	253·9	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{35}O)_2$	666	84·24
Oleic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{33}O)$	440	255·0	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{33}O)_2$	662	84·74
Linolic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{31}O)$	438	256·2	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{31}O)_2$	658	85·28
Linolenic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{29}O)$	436	257·3	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{29}O)_2$	654	85·78
Clupanodonic	$C_3H_5(O.C_2H_3O)_2(O.C_{18}H_{27}O)$	434	258·5	$C_3H_5(O.C_2H_3O)(O.C_{18}H_{27}O)_2$	650	86·3
Arachidic	$C_3H_5(O.C_2H_3O)_2(O.C_{20}H_{39}O)$	470	238·7	$C_3H_5(O.C_2H_3O)[O.C_{20}H_{39}O]_2$	722	77·7
Erucic	$C_3H_5(O.C_2H_3O)_2(O.C_{22}H_{41}O)$	496	226·2	$C_3H_5(O.C_2H_3O)(O.C_{22}H_{41}O)_2$	774	72·5
Cerotic	$C_3H_5(O.C_2H_3O)_2(O.C_{26}H_{51}O)$	554	202·5	$C_3H_5(O.C_2H_3O)(O.C_{26}H_{51}O)_2$	890	63·05
Melissic	$C_3H_5(O.C_2H_3O)_2(O.C_{30}H_{59}O)$	610	183·9	$C_3H_5(O.C_2H_3O)[O.C_{30}H_{59}O]_2$	1002	55·9
Ricinoleic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{32}O(O.C_2H_3O)]$	498	338·0	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{32}O(O.C_2H_3O)]_2$	778	216·3
Hydroxystearic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{34}O(O.C_2H_3O)]$	500	336·7	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{34}O(O.C_2H_3O)]_2$	782	215·3
Dihydroxystearic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{33}O(O.C_2H_3O)_2]$	558	402·2	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{33}O(O.C_2H_3O)_2]_2$	898	312·4
Trihydroxystearic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{32}O(O.C_2H_3O)_3]$	616	455·4	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{32}O(O.C_2H_3O)_3]_2$	1014	387·4
Sativic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{31}O(O.C_2H_3O)_4]$	674	499·3	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{31}O(O.C_2H_3O)_4]_2$	1130	446·8
Linusic	$C_3H_5(O.C_2H_3O)_2[O.C_{18}H_{29}O(O.C_2H_3O)_6]$	790	568·1	$C_3H_5(O.C_2H_3O)[O.C_{18}H_{29}O(O.C_2H_3O)_6]_2$	1362	535·5

The extent to which natural oils and fats become hydrolysed in course of time varies (see Chap. I.). Therefore, the amount of monoglycerides and diglycerides will vary accordingly; hence the acetyl value will likewise vary.

It follows, then, that in the case of the natural oils, fats, and waxes, with the exception of castor oil, the acetyl value will be a *variable*. It may be emphasised again that in the case of castor oil the acetyl value is a *characteristic*, because castor oil is practically a pure triglyceride of ricinoleic acid (or of its isomerides).

The acetyl value of those natural oils and fats which contain volatile or soluble fatty acids, as found by the above method, would include a certain amount of alkali absorbed by the volatile or soluble fatty acids described above. Therefore, without the necessary correction, the acetyl values found are too high, viz. by the amount due to the volatile acids. I have therefore termed the acetyl values found direct "*apparent acetyl values*." The *true* acetyl value is found by determining the amount of potash required to saturate the volatile acids of the original oil or fat in precisely the same manner, and deducting the number thus obtained from the apparent acetyl value[1] (cp. Chap. VIII. "Volatile Fatty Acids").

In the following table I give a list of a number of acetyl values determined by the above-described method, after deducting from the apparent acetyl values the amounts of potash required by the naturally-present volatile acids. The acetyl values contained in the following table represent, therefore, the *true acetyl values* :—

True Acetyl Values of Oils, Fats, and Waxes (Lewkowitsch)

Linseed	3·98
Candle nut	9·86
Safflower	16·1
Rape	14·7
Arachis	9·06
Hazel nut	3·2
Olive	10·64
Elderberry	15·5
Japanese sardine	13·0
Cod liver	4·8
Skate liver	10·6
Shark liver	11·9
Seal	16·5
Horses' foot	13·0
Neat's foot	22·0
Palm	18
Sawarri	7·0
Cacao butter	2·8

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[1] Thus recently J. Camo (*Bull. des Scienc. pharmacolog.*, 1908 (August), 442) found the *apparent* acetyl value of a specimen of oleander oil 30, whereas the *true* acetyl value was almost nil.

True Acetyl Values of Oils, Fats, and Waxes (Lewkowitsch)—continued

Palm nut	1·9-8·4
Cocoa nut	0·9-12·3
Japan wax	27-31·2
Lard	2·6
Beef marrow	4·2
Bone	11·3
Beef tallow	2·7-8·6
Butter	1·9-8·6
Sperm	4·5-6·4
Arctic sperm	4·1-6·4
Carnaüba wax	55·24
Wool wax	23·3
Beeswax	15·24
Spermaceti	2·63

These true acetyl values must not be looked upon as "characteristics," but as "variables," which furnish a measure of the amount of mono- and di-glycerides in the case of oils and fats, and of free alcohols in the case of waxes. They also include that amount of potash which is required for the saponification of the acetylated cholesterol or phytosterol (as the case may be).

The author has further pointed out[1] that the acetyl value may furnish a measure of the state of rancidity, if considered in conjunction with the acid value (see table, Chap. I. p. 57).

The acetyl value was first proposed by *Benedikt* as a "constant" (see p. 378) in the examination of oils and fats, and the process given by *Benedikt and Ulzer*[2] for its determination applied to the *insoluble fatty acids*, and not to the fats and oils themselves. In this process the authors determined first the amount of alkali required to neutralise 1 grm. of acetylated fatty acids—"acetyl acid value"—and further, in a second experiment, the amount of potash required both to saturate the free acid and to combine with the acetyl group split off on boiling with alcoholic potash—"acetyl saponification value." The difference of the two amounts of alcoholic potash was termed by *Benedikt* the "acetyl value."

The neutralisation and the saponification of the acetylated acids were, therefore, *supposed* to take place in two stages according to the following equations :—

1. $C_{17}H_{32}(O.C_2H_3O).COOH + KOH = C_{17}H_{32}(O.C_2H_3O)COOK + H_2O.$
   Acetyl-ricinoleic acid. Potassium salt.

2. $C_{17}H_{32}(O.C_2H_3O)COOK + KOH = C_{17}H_{32}(OH)COOK + C_2H_3O_2K.$
   Potassium acetyl-ricinoleate. Potassium ricinoleate.

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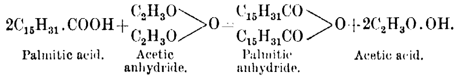
[1] Cp. Lewkowitsch, "The Meaning of the Acetyl Value in Fat Analysis," *Analyst*, 1899, 319.

[2] *Monatsh. f. Chem.*, 8, 40 ; cp. Lewkowitsch, 2nd edition of this work, 1898, p. 163.

The hydroxyl of the carboxyl group of the fatty acids should consequently not have been affected by the boiling with acetic anhydride during acetylation. Fatty acids containing no alcoholic hydroxyl group, such as stearic, oleic, etc., should therefore not yield an acetyl value, as the (neutralisation) acid and saponification values in these cases should be identical.

Lewkowitsch,[1] however, has shown that pure capric, lauric, palmitic, stearic, cerotic, and oleic acids exhibited very considerable acetyl values when treated according to *Benedikt and Ulzer's* process. This result can only be explained by the fact that part of the fatty acids had been converted into their anhydrides, the acetic anhydride acting in the manner explained by the following equation :—



$$2C_{15}H_{31}.COOH+\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\!>O=\begin{matrix}C_{15}H_{31}CO\\C_{15}H_{31}CO\end{matrix}\!>O+2C_2H_3O.OH.$$

The anhydrides were actually isolated by *Lewkowitsch*, and their great stability in presence of even boiling water was proved.[2]

When these anhydrides were dissolved in *cold alcohol* and standard caustic alkali was added, hydrolysis of the anhydrides took place at once to a certain extent, and as the fatty acid so formed combined with a definite amount of potash, an (apparent) acid value of the substance was obtained. When, however, the anhydrides were shaken up with *water*, the first drop of potash gave in the presence of phenolphthalein a pink colouration, which disappeared but slowly. This showed that in the *alcoholic* solution partial hydrolysis of the anhydrides took place, hydrolysis ceasing when an equilibrium was established in the solution. Under these conditions apparent acetyl values were obtained for capric, lauric, palmitic, etc., acids. Hence the acetyl numbers so found were, in truth, fictitious values.

Hydroxylated fatty acids are certainly acetylated (in their alcoholic OH group) when boiled with acetic anhydride, but simultaneously the acetylated acids are converted into their anhydrides owing to the large excess of acetic anhydride used. During the subsequent boiling with water, a portion of the anhydrides may, or may not, become hydrolysed, and thus a mixture of free acetylated acids and acetylated anhydrides is obtained.

When this mixture is dissolved in alcohol and titrated with caustic potash, after neutralisation of the free acids (if any), partial hydrolysis will set in, as explained above in the case of capric acid, etc., and an " acid value " will thus be obtained (*Benedikt's* " acetyl acid value "). But such " acid value " will be lower than the neutralisation value of the acetylated fatty acids, as the anhydrides remain unacted upon to a certain extent. Consequently the saponification value of the acetylated product (*Benedikt's* " acetyl saponification value ") will be found too high, since the non-hydrolysed anhydrides are subsequently saponified on boiling with alcoholic potash. The difference between "acetyl saponification" and "acetyl acid" values, supposed by *Benedikt* to be the acetyl value of the acids, is therefore devoid of any quantitative meaning.

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[1] *Proc. Chem. Soc.*, 1890, 72, 91 ; *Journ. Soc. Chem. Ind.*, 1890, 660.

[2] Cp. also the action of acetic anhydride on ricinoleic acid (p. 215).

The same conclusion, of course, holds good in the case of a mixture of hydroxylated and ordinary fatty acids.

It is therefore evident that the "acetyl values" found by various observers working according to *Benedikt and Ulzer's* method must be accepted with the greatest reserve.

Benedikt and Ulzer's method had been worked out with castor oil; and the satisfactory result found in this case led to a generalisation which must be considered inadmissible. Hence, most of the numbers contained in the older literature and stated to indicate the presence of hydroxylated fatty acids in natural oils and fats (with the exception of castor oil and, perhaps, grape seed oil[1] and quince oil) must be rejected as fictitious values.

It may be repeated, the acetyl value of a natural oil or fat will be a **characteristic** if *tri*glycerides only are present. Otherwise the acetyl value will be a **variable**, indicating, in addition to hydroxylated fatty acids, free alcohols (such as cholesterol or phytosterol) and also monoglycerides and diglycerides. In the latter event the acetyl value may be indicative of rancidity in an oil or fat. In the case of waxes the acetyl value indicates the presence of free alcohols. For the acetyl value of "blown oils" (oxidised oils), see Vol. III. Chap. XV., as also Chap. VIII. "Acetyl Value of Fatty Acids."

If a **free alcohol** is acetylated, no complication through formation of anhydrides can arise. The saponification value of the acetylated product—the acetate of the alcohol—represents also the acetyl value of the alcohol (the saponification value of the original alcohol being, of course, nil). (Cp. table, "Saponification Values of Waxes," p. 385.)

B. VARIABLES

1. Acid Value

The acid value indicates the number of milligrams of potassium hydrate required to saturate the free fatty acids in one gram of a fat or wax; or, in other words, *it gives the amount of potassium hydrate, expressed in tenths per cent, necessary to neutralise the free fatty acids in a fat or wax.*

The acid value is therefore a measure of the free fatty acids in a fat or wax.

In order to determine the acid value of a fat or wax the sample is mixed with alcohol (purified methylated spirit), or with methyl alcohol or amyl alcohol,[1] or a mixture of alcohol and ether,[2] and titrated with aqueous or alcoholic standard alkali, phenolphthalein being used as indicator.

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[1] See Vol. II. Chap. XIV. "Grape Seed Oil."

The standard alkali may be half-, or tenth-normal. If notable amounts of free fatty acids are present, it will be found convenient to titrate at first with half-normal alkali and to finish with a few drops of decinormal solution. Some analysts prefer an alcoholic standard solution to an aqueous one, although the accuracy of the analysis is *not* increased thereby, provided care be taken that the resulting soap solution contains at least 50 per cent of alcohol (see p. 135). On the contrary, an alcoholic standard solution has the drawback of altering its titer somewhat rapidly, and therefore errors are likely to occur unless the solution be standardised frequently. The end-point of titration is distinctly recognisable; saponification of the neutral fat does not take place immediately by the small excess of alkali necessary to produce the pink colouration. On standing, however, for some time, even if access of air (and consequent decolouration, due to absorption of carbonic acid) be precluded, the pink colour will disappear in some cases, owing to the neutral esters[3] undergoing saponification. This will be especially the case if the specimen under examination be dissolved in ether-alcohol. It would, obviously, be erroneous to add more alkali from time to time when the pink colouration disappears.

Mineral acid in the sample must, of course, be first removed by washing with water; all solvents employed should be free from substances giving an acid reaction. Before using the solvent, it will be best to neutralise it exactly with decinormal alkali, using phenolphthalein as an indicator.

Liquid fats are weighed off or measured off accurately in a flask, neutralised alcohol and a few drops of a 1 per cent solution of phenolphthalein are then added, and the liquid is titrated with constant shaking. Convenient quantities are 10 grms. (or 10 c.c.) of oil and 50 c.c. of alcohol.

Solid fats must be warmed with the alcohol on the water-bath until the fat is liquefied; they are then titrated in the same manner. Should the fat solidify during the operation, the flask must be warmed again before the titration can be brought to an end. To guard against partial saponification of the neutral fat, excess of alkali must be avoided. If it should be deemed preferable to work with clear solutions, the fat may be dissolved in a mixture consisting of two parts of ether and one part of alcohol, and then titrated with alcoholic standard solution.

One or two examples will illustrate the method of calculating the acid value.

1. Weighed off 3·254 grms. of tallow. Required for neutralising the free fatty acids 3·5 c.c. of decinormal caustic potash (or soda) or

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[1] Halphen, *Ann. chim. anal. appl.*, 1901 (6), 133.

[2] The suggestion to titrate in alcohol-benzene solution has been severely criticised by E. Boedtker (*Chem. Zeit.*, 1911, 548).

[3] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1890, 846.

3·5 × 5·61 milligrams KOH. The amount of KOH required for 1 grm. of tallow, *i.e.* its *acid value,* is therefore

$$A=\frac{3\cdot5\times5\cdot61}{3\cdot254}=6\cdot03.$$

2. Measured off 25 c.c. of olive oil, spec. grav. 0·917. Required for neutralising the free fatty acids 9·4 c.c. of a solution of caustic potash, 1 c.c. of which contains 0·0257 grms., or 25·7 milligrams KOH. The weight of the oil is 25 × 0·917 = 22·925 grms., therefore

$$A=\frac{9\cdot4\times25\cdot7}{22\cdot925}=10\cdot5.$$

The proportion of free fatty acids in an oil or fat is frequently expressed in a different manner.

In this country, especially in the case of oils, it is usual to calculate the free acid as oleic acid, molecular weight 282, and to express the amount of free fatty acids in per cent of the fat. Thus in the first example the percentage of free fatty acids would be returned as

$$\frac{3\cdot5\times0\cdot0282}{3\cdot254}\times100=3\cdot03\%,$$

and in the second example as

$$\frac{9\cdot4\times0\cdot0257\times0\cdot282}{0\cdot0561\times22\cdot925}\times100=5\cdot28\ \%.$$

Since the molecular weight of oleic acid, 282, is approximately five times 56·1 (the molecular weight of KOH), and the acid value expresses the amount of KOH in tenths per cent, a rapid and in most cases sufficiently accurate method of converting the acid value into per cent of oleic acid is to multiply the former by 0·5. In the case of cocoa nut and palm kernel oils this factor would, however, not be admissible; the calculation should be based on a mean molecular weight of 210 and 220 respectively.

In other cases (lubricating oils), the free fatty acids are sometimes expressed in terms of sulphuric anhydride, SO_3, and the result is given in per cent of the oil employed. Thus in the first example we should find

$$\frac{3\cdot5\times0\cdot004}{3\cdot254}\times100=0\cdot43\ \%,$$

and in the second

$$\frac{9\cdot4\times0\cdot0257\times0\cdot04}{0\cdot0561\times22\cdot925}\times100=0\cdot75\ \%.$$

Köttstorfer proposed to express the acidity by the number of c.c. of normal potash required for 100 grms. of the fat. In this connection the number of c.c. is termed "degree of acidity."

In the subjoined table a comparison is made of the different methods of expressing the acidity; an easy calculation allows of transforming one term into any other.

Acid Value, being $\frac{1}{10}$ per cent of KOH.	Oleic Acid. Per cent.	Sulphuric Anhydride. Per cent.	Degrees Köttstorfer, being c.c. normal KOH per 100 grms. Fat.
1	0·5027	0·0713	1·782
1·9893	1	0·1418	3·546
14·0250	7·0500	1	25·000
0·5610	0·2820	0·0400	1

The acid value is not a "characteristic," and the but too frequent references in the literature on our subject to this value as a "constant" (or "characteristic") are entirely misleading. The acid value of natural oils and fats is a **variable**, entirely depending on the state of purity of an oil, its age, the extent to which it has suffered hydrolysis, and the amount of oxidation it has undergone. In the case of fresh oils and fats (as has been pointed out already) the quantity of free fatty acid is so small that it may be considered negligible. Vegetable oils seem to contain small quantities of free fatty acids, whereas animal fats in the fresh state are practically devoid of free fatty acids (Chap. I. p. 43). It has also been pointed out that if oils and fats are left in contact with putrescible or fermentable matter, the amount of free fatty acids may rapidly increase, and rise to 70 and even to 100 per cent, as in the case of old palm oil (Chap. I. p. 50). The importance of the acid value lies, therefore, in the fact that it indicates the *quality* of an oil or fat. It shows the extent to which an oil or fat has undergone hydrolysis, and if this value be considered in conjunction with the acetyl value, it may indicate not only the amount of lower fatty acids that have been formed by destruction, but also the amount of oxidised acids formed subsequently, in the wake of hydrolysis.

In case the nature of the free acid, and consequently its molecular weight, be known, the absolute quantity of free acid may be calculated, as shown above for oleic acid. In such cases the table given below may be found useful.

Since the acid values are variables, no useful purpose would be served here by giving a list of those acid values of natural oils and fats that have been recorded. The numbers found in practice for such specimens as were submitted to examination will be given under the headings of the individual oils and fats in Vol. II. Chap. XIV.

In the case of waxes, the acid values vary in a smaller degree than in the case of oils and fats; a certain proportion of free fatty acids, varying within narrow limits, seems to be characteristic of carnaüba wax and beeswax (cp. Chap. I. and Vol. II. Chap. XIV.).

It is evident that if an oil or fat consists exclusively of neutral triglycerides, its acid value will be nil. In that case the saponification value will indicate the amount of caustic potash required to saponify the *neutral esters*, or, in other words, the amount of potash required to neutralise the combined fatty acids. But if the oils and fats contain free fatty acids, that is, if they exhibit a definite acid value, then the saponification value will be the sum of the amounts of caustic potash requisite to neutralise both the free fatty acids and those fatty acids which are combined with glycerol as esters. The difference between these two amounts of potash has been termed by *Hübl and Benedikt* " ester value " or " ether value," and was understood to indicate the number of milligrams of potassium hydrate required for the saponification of the neutral esters contained in one gram of an oil or fat. Those writers who termed the acid value a " constant " were naturally bound to consider the ether value also as a " constant." As I have shown that the acid value is a *variable*, it is obvious that the " ester value " also must be a *variable*. This is exemplified by the following table, part of which has been given above :—

Variations of Saponification and " Ester " Values

Stearin. Per cent.	Stearic Acid. Per cent.	Saponification Value.	Acid Value.	" Ester " Value.
100	0	189·1	0	189·1
75	25	191·02	49·37	141·65
50	50	193·30	98·75	94·55
25	75	195·41	148·13	47·28
0	100	197·5	197·5	0

But even with these restrictions, the " ester value " can only have a meaning in the absence of mono- and di-glycerides. Since, however, the presence of free fatty acids points to hydrolysis of neutral triglycerides having taken place, and since it is this hydrolysis which is the cause of the presence of mono- and di-glycerides, the so-called " ester value " loses its meaning also in this case, inasmuch as that part of the caustic potash which is required for the saponification of the esters refers to a mixture of triglycerides, diglycerides, and monoglycerides. Hence it follows that all the references in the chemical literature to " ester values " of oils and fats are more or less valueless.

In the solid waxes—carnaüba wax and beeswax—the acid value varies, as stated above, within somewhat definite limits; hence the " ester value " likewise varies within definite limits, and therefore a certain amount of importance has been attached to the " ester value " in the analysis of beeswax. But since even in these instances the " ester value " is merely a figure obtained by the difference of two numbers (saponification value *minus* acid value), it is unnecessary to introduce a new term. Therefore, even in the case of waxes, reference to an " ester value " will be omitted.

2. Glycerol

According to the fundamental equation, in which R stands for the radicle of any fatty acid—

$$C_3H_5(OR)_3 + 3KOH = C_3H_8O_3 + 3KOR.$$

3 molecules of caustic potash are required for the saponification of 1 molecule of neutral fat, yielding 1 molecule of glycerol. Therefore, for every 168·3 grms. of KOH used, 92 grms. of glycerol will be obtained; consequently 1 grm. of KOH is equivalent to 0·54664 grm. of glycerol.

In the case of pure triglycerides, the proportion of glycerol is a "characteristic" (cp. following table), and the quantity of glycerol yielded by an oil or fat can be calculated from the saponification value as shown. In the case of natural oils and fats, a calculation of this kind will lead to erroneous results, not only on account of the small quantities of "unsaponifiable matter" that are always present, but chiefly on account of the free fatty acids and mono- and di-glycerides, which occur in natural oils and fats in variable quantities. Therefore the percentage number of glycerol must be looked upon as a "*variable*" in the case of natural oils and fats.

This "variable" stands to the acid value in the relation that the higher the acid value, the smaller is the yield of glycerol, whereas the larger the proportion of mono- and di-glycerides the larger is the proportion of glycerol.

It may further be pointed out that the higher the saponification value of an oil or fat the larger is the amount of glycerol it yields. Hence the fats belonging to the cocoa nut oil group yield more glycerol than those having a saponification value in the neighbourhood of 195, such as tallow and lard.

In the following table the proportion of glycerol yielded by mono- and di-glycerides is placed side by side with that yielded by triglycerides:—

Percentages of Glycerol obtained on saponifying Tri-, Di-, and Mono-glycerides

Glyceride of Acid.	Triglyceride.	Diglyceride.	Monoglyceride.
Acetic	42·20	52·27	68·65
Butyric	30·46	39·66	56·80
Valeric	26·74	35·38	52·27
Caproic	23·96	31·94	48·42
Caprylic	19·58	26·74	42·20
Capric	16·67	23·00	37·40
Lauric	14·42	20·18	33·58
Myristic	12·74	17·97	30·46
Palmitic	11·42	16·20	27·88
Stearic	10·34	14·74	25·70
Oleic	10·41	14·84	25·85
Linolic	10·48	14·93	25·99
Linolenic	10·55	15·03	26·14
Clupanodonic	10·62	15·13	26·28
Ricinoleic	9·87	14·11	24·74
Arachidic	9·45	13·52	25·83
Erucic	8·74	12·57	22·33
Cerotic	7·50	10·85	19·58
Melissic	6·60	9·79	17·49
Hydroxystearic	9·81	14·03	24·60
Dihydroxystearic	9·33	13·37	23·59
Trihydroxystearic	8·90	12·78	22·66
Sativic	8·51	12·24	21·80
Linusic	7·81	11·28	20·26
Mixed Triglycerides—			
Acetodiformin	48·4		
Acetodibutyrin	33·6		
Myristopalmitoölein	11·4		
Oleodipalmitin (Dipalmitoölein)	11·06		
Stearodipalmitin (Dipalmitostearin)	11·03		
Oleopalmitostearin (Stearopalmitoölein)	10·69		
Palmitodistearin (Distearopalmitin)	10·67		
Oleodistearin	10·4		
Elaïdodistearin	10·4		
Dioleostearin	10·38		

For the determination of the proportion of glycerol which a fat yields on saponification a considerable number of methods have been proposed. (It would be incorrect to speak of the proportion of glycerol in a fat, since glycerol is only formed on saponification by assimilation of water.)

The older processes, which aimed at the isolation of glycerol, so as to weigh it in substance (as was done in *Chevreul's* original method), are not accurate enough for quantitative purposes. On the one hand they yield results below the truth, owing to volatilisation of small amounts of glycerol at 100° C. (p. 244). (This source of error is avoided in *David's* process,[1] in which the concentration of the glycerol solution is not carried so far that loss is incurred, but it introduces another error through the necessity of saponifying with barium hydrate ; cp. p. 103.) On the other hand the product so obtained is always contaminated with foreign substances, and therefore too high results are obtained.

A direct method for determining glycerol in oils and fats (as also in commercial glycerins), by isolating it in substance, has been worked out by *Shukoff and Schestakoff*.[2] It is necessary to operate with a solution containing at least 40 per cent of glycerol. If the solution be more dilute, a quantity corresponding to about one gram of glycerol is carefully evaporated on the water-bath, avoiding of course loss by volatilisation, *i.e.* a concentration of about 50 per cent must not be exceeded. Before evaporating, the solution is rendered slightly alkaline with potassium carbonate. The concentrated solution is then mixed with 20 grams of ignited and powdered anhydrous sodium sulphate and extracted in a *Soxhlet* extractor with anhydrous acetone (previously well dried over ignited potassium carbonate). As acetone attacks both cork and india-rubber, all connections must be made with ground-glass fittings. The extraction requires a somewhat lengthy time. *Shukoff and Schestakoff* directed to extract four hours, but later observers maintain that this is not sufficient for the complete extraction. Thus *Landsberger* [3] demands no less than nine hours, whilst the chemists of the *Schlebusch Factory* [4] consider that only five to six hours are required. Should some oil float on the top of the acetone solution, it must be removed by washing with low boiling petroleum ether. The glycerol solution is then carefully dried in an air-bath, at a temperature not exceeding 75° to 80° C. until the weight is nearly constant. The chemists of the *Schlebusch Factory*, however, maintain that the temperature of the drying oven should be 90° to 95° C. (for two hours). The analyses published by *Shukoff and Schestakoff* exhibit very good agreement with the results obtained by the methods described below, whereas the above-named observers found somewhat high results. This may be due to the acetone having extracted some foreign substances. Whilst the time required for a determination may prove somewhat long for practical purposes, the method will be found useful in all those cases where it is desirable to isolate the glycerol.

Before *Shukoff and Schestakoff's* method can find general acceptance, further examination seems to be desirable.[5] Meanwhile, most commercial determinations of glycerol in oils and fats are carried out by indirect methods.

(1) *Determination of Glycerol by Oxidation Processes*

By oxidation with potassium permanganate in a strongly alkaline solution at the ordinary temperature, glycerol is converted quantitatively into oxalic acid, carbon dioxide, and water, according to the following equation :—

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[1] *Compt. rend.*, 1882, 94, 1477.

[2] *Zeits. f. angew. Chem.*, 1905, 294.

[3] *Chem. Revue*, 1905, 150.

[4] *Zeits. f. angew. Chem.*, 1905, 1656.

[5] Cp. S. Fachini and G. Dorta, *Boll. Chim. Farm.*, 1910 (49), 237. G. Beis, *Bull. Soc. Chim. de France*, 1912 (11), 618.

$$C_3H_8O_3+3O_2=C_2H_2O_4+CO_2+3H_2O.$$

This reaction, originally suggested by *Wanklyn and Fox*,[1] has been worked out as a basis for a quantitative method by *Benedikt and Zsigmondy*[2] in the following manner :—Saponify 2 to 3 grms. of the sample of fat with caustic potash and pure methyl alcohol, evaporate off the alcohol, dissolve the soap in hot water, and decompose with dilute hydrochloric acid. Then warm until the liberated fatty acids have separated out as a clear oily layer. In the case of a liquid fat some paraffin wax is best added so as to obtain a solid cake after cooling. Next filter into a spacious flask, wash well, and neutralise with caustic potash, using methylorange as an indicator. Then add 10 grms. of caustic potash in sticks, and run in a 5 per cent solution of potassium permanganate, until the liquid no longer appears green, but strongly pink or blackish. Instead of a solution, finely powdered potassium permanganate crystals may be used. Next heat the liquid to the boiling point,[3] when hydrated manganese dioxide separates, and the solution becomes red ; discharge the colour by adding carefully sulphurous acid solution required (but not more) for the reduction of the excess of the permanganate, taking care that the solution still remains strongly alkaline. Filter through a plain filter of sufficiently large size to hold at least one-half of the liquid, and wash the precipitate well with boiling water. It may happen that small quantities of hydrated manganese dioxide pass through the filter with the last wash-waters, but this does not at all interfere with the accuracy of the process.

Acidify the filtrate with acetic acid, whereby sufficient sulphurous acid is set free to reduce the manganese dioxide, heat the solution, which should have a volume of about 600 to 1000 c.c., almost to the boiling point, and precipitate with 10 c.c. of a 10 to 12 per cent solution of calcium chloride or calcium acetate. (If more of the precipitant be used, considerable quantities of calcium sulphate are thrown down, which are apt to vitiate the quantitative determination.) The precipitate contains silicic acid in addition to calcium oxalate ; hence the amount of oxalic acid cannot be calculated from the weight of the calcium carbonate (or calcium oxide) obtained on ignition. The amount of oxalic acid must therefore be either determined volumetrically, or inferred by titrating the ignited residue. In the latter case dissolve the ignited precipitate in an accurately measured excess of half-normal hydrochloric acid, and titrate with half-normal caustic soda, using methylorange as an indicator. Eighty parts of sodium hydrate are equivalent to 92 parts of glycerol.[4]

Allen[5] somewhat modified this process by suggesting the following

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[1] *Chem. News*, 53, 15.

[2] *Journ. Soc. Chem. Ind.*, 1885, 610.

[3] It is not advisable to keep the solution at the boiling point for any length of time.

[4] Cp. also A. Beythien, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1911 (xxi.), 673.

[5] *Commercial Organic Analysis*, ii. 290.

modus operandi :—The fat is saponified with aqueous caustic potash in a closed flask. The oxidation is effected as described above, except that sodium sulphite is used for reducing the excess of permanganate. The liquid containing the precipitated hydrated peroxide of manganese is then poured into a 500 c.c. flask, made up to 500 c.c.; 15 c.c. of hot water are added above the mark, as an allowance for the volume of the precipitate and for the expansion of the hot liquid. The solution is next poured through a dry filter, and 400 c.c. of the filtrate, when cold, are measured off accurately, acidulated with acetic acid, and precipitated with calcium chloride. The precipitate is filtered off, washed well, and rinsed into a porcelain dish after piercing the filter. The neck of the funnel is then plugged, and the filter filled with dilute sulphuric acid, which, after standing for a few minutes, is allowed to run into the dish. Sufficient sulphuric acid is next added to bring up the total amount of acid to a quantity equal to 10 c.c. of concentrated sulphuric acid, when the solution is warmed to 60° C. and titrated with potassium permanganate. If decinormal permanganate be used, each c.c. corresponds to 0·0045 grm. of oxalic acid ($C_2H_2O_4$), or to 0·0046 grm. of glycerol.

With regard to this process the following notes will be found useful :—Methyl alcohol is used in the saponification of the fat instead of ethyl alcohol, as the latter may, under certain conditions of concentration, give rise to the formation of oxalic acid. The errors resulting from this cause increase with the amount of alcohol retained by the soap on evaporation. On the other hand, if complete elimination of the alcohol be attempted by repeated boiling down of the dissolved soap, loss of glycerol may result.

The liquid treated with permanganate contains besides glycerol, the soluble fatty acids originally combined with it in the fat. By working strictly according to the directions given above, neither oxalic acid nor any other organic acid, yielding a calcium salt insoluble in acetic acid, will be formed. Therefore, it may be safely inferred that the presence of soluble fatty acids does not interfere with the correctness of the determination. *Johnstone*,[1] it is true, maintained that the process is useless in presence of butyric acid, as this acid is nearly all converted into oxalic acid, but both *Hehner*[2] and *Mangold*[3] have shown that in the process as carried out according to the directions of *Benedikt and Zsigmondy* no oxalic acid is formed. An explanation of *Johnstone's* error may be found in *Berthelot's* observation (re-stated by *Mangold*), that butyric acid yields oxalic acid when boiled for a considerable time with an excess of potassium permanganate.

An excess of sulphurous acid must be carefully avoided, since in presence of hydrated peroxide of manganese, sulphurous acid oxidises the oxalic acid formed. This error is obviated by *Allen's* proposal to use sodium sulphite instead of sulphurous acid. If the hydrated peroxide be removed by filtration, and the solution be acidified with acetic acid, no further action on the once-formed oxalic acid takes place. But since towards the end of the washing operations small quantities of the peroxide pass through the filter, and are reduced by the sulphurous acid set free by the acetic acid, and, moreover, since small quantities of calcium sulphite may be admixed with the precipitated calcium oxalate, it would be best to avoid altogether the use of sulphurous acid or of a sulphite.

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[1] *Journ. Soc. Chem. Ind.*, 1891, 204.

[2] *Ibid.*, 1891, 204.

[3] *Ibid.*, 1891, 803.

Herbig,[1] therefore, substitutes hydrogen peroxide for the sulphite; he further recommends the use of a smaller quantity of potassium permanganate. *Herbig's* method has been examined by *Mangold*,[2] and the following modification of the *Benedikt-Zsigmondy* process has been recommended by him as yielding reliable results:—2 to 4 grms. of fat are saponified; the filtrate from the liberated fatty acids is placed in a litre flask, diluted to 300 c.c., and 10 grms. of potassium hydrate are added, and as much of a 5 per cent permanganate solution as will correspond to *one and a half* times the theoretical quantity required for the oxidation of the glycerol (6·87 parts of MnO_4K being the amount required by theory for *one* part of $C_3H_8O_3$). This operation is conducted in the *cold* and with constant shaking. Allow to stand for half an hour at the ordinary temperature, and add sufficient hydrogen peroxide (avoiding, however, a large excess) to decolourise the liquid completely. Then make up to 1000 c.c., shake well, and filter 500 c.c. through a dry filter. Boil the filtrate for half an hour to decompose all hydrogen peroxide, allow to cool to 60° C., acidify with sulphuric acid, and titrate with standard permanganate solution. In a later publication *Herbig*[3] points out that cork and india-rubber connections should be avoided, as they give rise to the formation of oxalic acid.

If the glycerol solution contain any other substance yielding oxalic acid on oxidation, as is notably the case with oxidised linseed oil and oxidised oils in general, the *Benedikt-Zsigmondy* process is, of course, useless. In the preparation of glycerol from commercial oils and fats, the glycerol solution is always more or less contaminated with impurities which may, or may not, lead to the formation of oxalic acid. This uncertainty robs the permanganate method of its usefulness to a great extent.

Still more uncertain are the methods based on the oxidation of glycerol with potassium permanganate in acid solution whereby glycerol is oxidised to carbon dioxide and water, according to the following equation:—

$$C_3H_8O_3+7O=3CO_2+4H_2O.$$

If chemically pure glycerol be oxidised, the method will, of course, lead to correct results; but in all other cases the results are so misleading that I consider it unnecessary to describe the methods proposed under this head.[4]

For, whereas in the *Benedikt-Zsigmondy* method erroneous results are only obtained in the presence of organic substances which yield oxalic acid, oxidation in acid solution leads to far greater errors, since any other organic substances present also yields carbonic acid, and therefore renders the determination practically useless.

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[1] *Inaug. Dissert.*, Leipzig, 1890.

[2] *Zeits. f. angew. Chem.*, 1891, 400.

[3] *Chem. Rev.*, 1903, 9.

[4] See second edition of this work, p. 211.

Identical in principle with the last-named methods are the processes based on the oxidation of glycerol by means of potassium bichromate. Since the employment of potassium bichromate readily admits of the application of volumetric methods, oxidation by means of potassium bichromate has been recommended by several chemists.[1] Other oxidising agents were proposed by *Chaumeil* (iodic acid), by *Gailhat* (permanganate in presence of manganese sulphate), and by *Henkel and Roth*[2] (chromic acid). The strictures pointed out above would apply to all these proposals (*Lewkowitsch*[3]).

(2) *Determination of Glycerol by the Acetin Process*

The glycerol obtained in the saponification of a fat is necessarily more or less impure; hence *Lewkowitsch*[4] recommends to prepare crude glycerin in a manner similar to that employed on a large scale, and to determine accurately the proportion of glycerol by the *Benedikt-Cantor*[5] acetin process.

Twenty grams of an oil or fat are saponified in the usual manner, with alcoholic potash, and the alcohol is driven off on a water-bath. The resulting soap is decomposed with sulphuric acid and the liberated fatty acids are filtered off. The filtrate is neutralised with an excess of barium carbonate and boiled down on the water-bath until most of the water is driven off. The residue is exhausted with a mixture of ether and alcohol, the ether-alcohol driven off for the most part by gently heating on the water-bath, and the residue left is dried in a desiccator and weighed. It is not necessary to dry until constant weight is obtained, as the actual glycerol present is determined in the crude product by the acetin method.

This process is based on the quantitative conversion of glycerol into triacetin (p. 431), by heating concentrated glycerol with acetic anhydride. If the product of this reaction is then dissolved in water, and the free acetic acid has been carefully neutralised with alkali, the dissolved triacetin can be easily estimated by saponifying with a known volume of standard alkali and titrating back the excess. The solutions required are—

1. Half-normal or normal hydrochloric acid (*accurately* standardised).
2. Dilute caustic soda, containing about 20 grms. of NaOH in 1000 c.c. Its exact strength need not be known, but care should be taken that it be practically free from carbonate.
3. A 10 per cent solution of caustic soda.

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[1] Richardson and Jaffé, *Journ. Soc. Chem. Ind.*, 1910, 198.

[2] *Zeits. f. angew. Chem.*, 1905, 1936.

[3] *Analyst*, 1903, 107.

[4] *Chem. Zeit.*, 1889, 659.

[5] *Journ. Soc. Chem. Ind.*, 1888, 696; cp. Lewkowitsch, *ibid.*, 1889, 574; *Chem. Zeit.*, 1889, 13; 93; 191; 659; Hehner, *Journ. Soc. Chem. Ind.*, 1889, 6.

Solutions 2 and 3 are best kept in large bottles connected by means of syphon tubes with burettes, so that the latter may be filled automatically. To prevent absorption of carbon dioxide from the air, the bottles are provided with soda-lime tubes through which the air enters.

The estimation is carried out as follows :—

About 1·5 grms. of crude glycerin, weighed off accurately, are heated with 7-8 c.c. of acetic anhydride and 3 grms. of anhydrous sodium acetate (carefully dried in an oven) for $1\frac{1}{2}$ hours in a round-bottomed flask, of about 100 c.c. capacity, connected with an inverted condenser. The mixture is then allowed to cool a little, 50 c.c. of recently boiled warm water are poured down through the tube of the condenser, and the acetin is made to dissolve by shaking the flask ; if necessary, the contents of the flask may be slightly warmed, but must not be boiled. As triacetin is volatile with water vapours, these operations should be carried out whilst the flask is still connected with the condenser. The solution is next filtered from a flocculent precipitate containing most of the impurities of the crude glycerin, into a wide-mouthed flask of about 500-600 c.c. capacity, and washed with recently boiled water ; the filtrate is allowed *to cool down* to the ordinary temperature. Phenolphthalein is then added, and the free acetic acid neutralised with the dilute caustic soda solution. Whilst running this in, the solution must be agitated continually, so that the alkali may not be in excess *locally* longer than is unavoidable. The point of neutrality is reached when the slightly yellowish colour of the solution just changes into reddish-yellow. If the solution is allowed to become pink, the point of neutrality has been exceeded, and a fresh test must be made ; the excess of soda cannot be titrated back, as partial saponification of the acetin takes place in presence of the slightest excess of alkali. The change of colour is very characteristic, and is easily recognised after some little practice.

25 c.c. of the strong soda solution are now run in and the solution is boiled for a quarter of an hour ; the excess of soda is then titrated back with the standard acid. Side by side, operating in the same manner, 25 c.c. of the strong caustic soda solution are boiled and titrated with acid. The difference between the two titrations corresponds to the amount of alkali required for the saponification of the triacetin formed. From this the quantity of glycerol in the sample can be calculated, as shown by the following example :—Suppose 1·324 grms. of the sample have been treated as described above. Let 25 c.c. of the strong soda solution require 60·5 c.c. of normal hydrochloric acid, and let the number of c.c. required for titrating back the excess of soda be 21·5 ; then $60{\cdot}5 - 21{\cdot}5 = 39{\cdot}0$ c.c. have been used. 1 c.c. of normal acid corresponds to $\frac{0{\cdot}092}{3} = 0{\cdot}03067$ grm. of glycerol. Hence the sample contained $0{\cdot}03067 \times 39 = 1{\cdot}1960$ grms. or 90·3 per cent of glycerol. This is then referred and calculated to the amount of crude glycerin obtained on saponifying the original quantity of 20 grms. of oil or fat.

(3) *Determination of Glycerol as Isopropyliodide*

Zeisel and Fanto[1] proposed to determine glycerol by converting it into isopropyliodide. The method is based on the reaction expressed by the following equation :—

$$C_3H_5(OH)_3+5HI=C_3H_7I+3H_2O+2I_2.$$

The glycerol is converted (cp. Chap. III.), by means of hydriodic acid of specific gravity 1·7 (or even 1·9), in the presence of red phosphorus, into isopropyliodide, which is distilled over and received in an alcoholic solution of silver nitrate. The free iodine is retained by the red phosphorus. The iodine, distilled over in the form of isopropyliodide, is precipitated as silver iodide. Each molecule of silver iodide (AgI) is calculated to one molecule of glycerol (cp. Chap. III. p. 263).

The test is carried out in a special apparatus. The author[2] made two series of experiments on crude 80 per cent glycerin, but the results were found so much below the truth that he felt unable to recommend this method.

Later observers state that, provided the dilution of the glycerol solution is very high, satisfactory results are obtained. This is especially holding good of the determination of glycerol in fermented liquors, and the published results furnishing duplicate analyses are apparently very satisfactory. Yet it must be maintained that in these cases there is no proper and satisfactory check on the results obtained, as, obviously duplicate analyses, however well agreeing amongst themselves, do not prove the correctness of the result itself. *Fanto*[3] endeavoured to vindicate the *Zeisel and Fanto* method by giving a number of glycerol determinations in fats by a somewhat modified process. He saponifies 10 grms. of fat and then dilutes the glycerol solution down to 100 c.c., of which 5 c.c. are taken for the determination. Thus only about 0·05 grms. of glycerol are subjected to the process, and any error is multiplied by 20. Hence it would not be correct to accord excessive importance to the apparently correct percentage of glycerin obtained by this method. More recently *R. Wilstätter and A. Madinaveitia*[4] experimented with *Zeisel and Fanto's* method, working with 20 grms. of fat and hydriodic acid of 1·9 specific gravity. In their opinion it is not permissible to use a hydriodic acid of specific gravity 1·7, inasmuch as the fats are in that case incompletely hydrolysed and the proportion of glycerol therefore found too low. *Wilstätter and Madinaveitia* maintain that the method gives reliable results when a hydriodic acid of 1·8 specific gravity and no more than 0·15 to 0·35 grm. of fat are used. In support of this, analyses are given for " tristearin " and " triolein " (as to the purity of which no statement is made). The results as calculated by the present writer fluctuate between 95·6 to 98·7 per cent of the theoretical amount. It is obvious that by multiplying the analytical data by such enormous factors as 300 to 600, small unavoidable errors of the method become very considerably enhanced. The same authors give as further confirmation two analyses of glycerin from sesamé oil and "margarine." These, however, prove nothing, as the composition of different specimens of sesamé oil varies; moreover, the amount of glycerin found is decidedly too low. Since "margarine" fluctuates in its composition very widely, this analysis must be ruled out altogether, even if the difference between the duplicate analyses did not amount in per cent to 6·4.

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[1] *Zeits. f. d. landwirt. Versuchswesen in Oest.*, 1902.

[2] Lewkowitsch, *Analyst*, 1903, 108 ; cp. Buchner and Meisenheimer, *Berichte*, 1906, 3211. *Beihefte zu Veröffentl. des Kais. Gesundheitsamtes*, Berlin, 1911, p. 19.

[3] *Zeits. f. angew. Chem.*, 1904, 420.

[4] *Berichte*, 1912, 2825.

The tediousness of the *Zeisel-Fanto* method and the danger of multiplying small errors by large factors must naturally militate against its general applicability. Possibly the method may give good results in the case of chemically pure glycerin, but for that purpose more expeditious methods are available (see Vol. III. Chap. XV.).

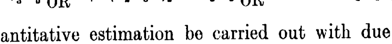
Buisine[1] recommends the estimation of glycerol by the method which he worked out for the determination of the higher alcohols in beeswax (see Chap. IX. p. 605). It is obvious that this method is too cumbersome when compared with those that have stood the test of practical experience.

3. Diglycerides and Monoglycerides

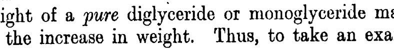
The occurrence of lower glycerides in a fat has hitherto been proved in a direct manner in the solitary case of rape oil by the isolation of dierucin (cp. Chap. I. p. 43; Chap. II. p. 77).

It has been shown (cp. Chap. I.) that we may expect the presence of di- and mono-glycerides in oils and fats containing small quantities of free fatty acids. The author demonstrated this to be actually the case by proving, in an indirect manner, the occurrence of di- and monoglycerides in partially saponified oils and fats (Chap. II. p. 72).

To detect di- and mono-glycerides in an oil or fat, the author boils an accurately weighed quantity of the sample with acetic anhydride, and washes the resulting product with boiling water until it is freed from acid. In the presence of notable quantities of di- and monoglycerides an increase of weight will be found. This is due to one or two acetyl groups, respectively, having been assimilated by one molecule of diglyceride or monoglyceride, as is shown by the following equations:—

1. 

$$C_3H_5\begin{matrix}OH\\(OR)_2\end{matrix}+(C_2H_3O)_2O=C_3H_5\begin{matrix}O\,.\,C_2H_3O\\(OR)_2\end{matrix}+C_2H_4O_2.$$

2. 

$$C_3H_5\begin{matrix}(OH)_2\\OR\end{matrix}+2(C_2H_3O)_2O=C_3H_5\begin{matrix}(O\cdot C_2H_3O)_2\\OR\end{matrix}+2C_2H_4O_2.$$

If the quantitative estimation be carried out with due care, the molecular weight of a *pure* diglyceride or monoglyceride may be calculated from the increase in weight. Thus, to take an example, if *a* grms. of a pure diglyceride have been weighed off, and an increase of weight, *i*, has been found, we have the proportion

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[1] *Compt. rend.*, 1903 (136), 1082.

$$a : a+i = M : M+42,$$

where M is the molecular weight of the diglyceride, and consequently M + 42 the molecular weight of the triglyceride obtained on assimilating the group $C_2H_2O(=42)$. The above proportion is expressed by the equation $a(M+42) = M(a+i)$; hence

$$M = \frac{42a}{i}.$$

As a rule, however, the diglyceride will only form a small proportion of the fat under examination. If the chemical composition of the diglyceride be known, the absolute quantity of the diglyceride in the sample may be calculated with the help of the equation

$$a = \frac{Mi}{42}.$$

Thus, if *b* grms. of a fat, containing a diglyceride of the known molecular weight M, have been weighed off, and the increase *i* was obtained on acetylating, the percentage *x* of the diglyceride in the sample will be found from the proportion

$$b : \frac{Mi}{42} = 100 : x;$$

hence

$$x = \frac{100Mi}{42b}.$$

The proportion of diglyceride can also be found volumetrically, if the molecular weight of the diglyceride be known. If M be the molecular weight of the diglyceride, K the saponification value of the sample under examination, and C the saponification value of the acetylated product, then the percentage D of the diglyceride may be calculated from the following formula (56·1 being the molecular weight of KOH and 42 that of C_2H_2O):

$$D = \frac{100(C-K)M.(M+42)}{56 \cdot 1(M-84)},$$

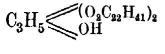
at which I arrive as follows: M grms. of a diglyceride require 2 × 56·1 grms. of KOH for saponification; M + 42 grms. of the triglyceride, obtained from it on digestion with acetic anhydride, require 3 × 56·1 grms. KOH. Therefore 1 grm. of the diglyceride requires $\frac{2 \times 56 \cdot 1}{M}$, and 1 grm. of the triglyceride $\frac{3 \times 56 \cdot 1}{M+42}$.

The difference

$$\frac{3 \times 56 \cdot 1}{M+42} - \frac{2 \times 56 \cdot 1}{M} = \frac{56 \cdot 1(M-84)}{M(M+42)}$$

will, in the case of a pure diglyceride, be practically equal to C − K, hence

$$D = \frac{100(C-K)M.(M+42)}{56 \cdot 1(M-84)}.$$

Thus if the proportion of dierucin,  $C_3H_5 \begin{cases} (O_2C_{22}H_{41})_2 \\ OH \end{cases}$ (M = 732) in "rape oil stearine" is required, and K be found = 158·4 for this rape oil stearine, and C = 180·2 for the acetylated rape oil stearine, we have, since C - K = 21·8,

$$D = \frac{100 \times 21{\cdot}8 \times 732 \times 774}{56{\cdot}1 \times (732 - 84)} = 34.$$

The correctness of this calculation may be proved as follows :—

The saponification value of pure dierucin $C_3H_5(OC_{22}H_{41}O)_2(OH)$ is 153·3, that of acetylated dierucin $C_3H_5(OC_2H_3O)(OC_{22}H_{41}O)_2$ is 217·4. The difference 217·4 - 153·3 = 64·1; found C - K = 21·8; therefore

$$D = \frac{21{\cdot}8 \times 100}{64{\cdot}1} = 34.$$

In case the amount of free fatty acids in an oil or fat is considerable, anhydrides of the fatty acids may be formed on boiling with acetic anhydride, whereby a decrease in weight is incurred; this decrease may, however, be obliterated by a simultaneous increase due to the presence of small quantities of mono- and di-glycerides.

Since complete hydrolysis of the anhydrides formed in the acetylating process is not obtained readily, it is necessary to remove first the free fatty acids, if their amount be considerable, by converting them into their potassium salts by titration with standard potassium hydrate, using phenolphthalein as an indicator, and extracting the glycerides with ether.

If the free fatty acids contain soluble fatty acids, whilst at the same time the amount of total free fatty acids is inconsiderable, then it is necessary to wash the sample with hot water until the soluble fatty acids have been removed.

It should be distinctly understood that the above-given calculations hold good only in the absence of free fatty acids and monoglycerides.

Since glycerides of hydroxylated fatty acids assimilate an acetyl group (or acetyl groups) on being digested with acetic anhydride, it is necessary, in the presence of such glycerides, to prepare the insoluble fatty acids and determine their acetyl value (see Chap. VIII.). Thus the difficulty caused by the presence of lower glycerides is removed.

From the acetyl value of the fatty acids a measure of the hydroxylated acids is obtained (Chap. VII.), and by introducing the most likely molecular weight, their absolute weight can be obtained and calculated to glycerides.

Oils and fats containing notable quantities of mono- and diglycerides furnish higher saponification values than their corresponding triglycerides, and consequently yield lower proportions of insoluble fatty acids (see Chap. VIII.). This will be seen by reference to the tables giving the respective values for monoglycerides and diglycerides.

When oils and fats are acetylated, the decrease in the proportion of insoluble fatty acids becomes still more pronounced, whilst the saponification values rise, as will be seen from the following table, in which I collate the corresponding values for the three most important mono- and di-glycerides :—

Glyceride of Acid.	ACETYLATED MONOGLYCERIDE.				ACETYLATED DIGLYCERIDE.				TRIGLYCERIDE.			
	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids. Per cent.	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids. Per cent.	Formula.	Molecular Weight.	Saponification Value.	Insoluble Fatty Acids. Per cent.
Palmitic	$C_3H_5(O.C_2H_3O)_2$ $O.C_{16}H_{31}O$	414	406·6	61·83	$C_3H_5(O.C_2H_3O)$ $(O.C_{16}H_{31}O)_2$	610	276·0	83·92	$C_3H_5(O.C_{16}H_{31}O)_3$	806	208·8	95·29
Stearic .	$C_3H_5(O.C_2H_3O)_2$ $O.C_{18}H_{35}O$	442	380·8	64·26	$C_3H_5(O.C_2H_3O)$ $(O.C_{18}H_{35}O)_2$	666	252·7	85·28	$C_3H_5(O.C_{18}H_{35}O)_3$	890	189·1	95·73
Oleic .	$C_3H_5(O.C_2H_3O)_2$ $O.C_{18}H_{33}O$	440	382·4	64·07	$C_3H_5(O.C_2H_3O)$ $(O.C_{18}H_{33}O)_2$	662	254·3	85·18	$C_3H_5(O.C_{18}H_{33}O)_3$	884	190·4	95·70

As a rule, however, we cannot derive (for practical purposes) distinct indications from the saponification values and the proportions of insoluble fatty acids, since in the presence of small quantities of mono- and di-glycerides the differences may fall within the errors of the method.

The same strictures would apply in a more forcible manner to the formula given by *Freundlich*[1] for the calculation of the proportion of diglycerides in oils and fats containing hydroxylated acids or their glycerides, without having recourse to the acetylating process. The use of this formula would lead to unjustified assumptions and conjectures, if, in consequence of unavoidable errors, somewhat low values were found; errors would notably occur in the proportion of insoluble fatty acids, owing to the experimental errors attaching to their method of determination. Hence I omit here *Freundlich's* formula.[2]

4. Unsaponifiable Matter

The term "unsaponifiable matter," like many terms borrowed from practice, is somewhat ambiguous.

I comprise here in the term "unsaponifiable matter" all those substances that are insoluble in water, or do not combine with caustic alkalis to form soluble soaps. Strictly speaking, glycerol itself, not being saponifiable by alkalis—just like the wax alcohols—is "unsaponifiable," and in this strict sense only the fatty acids are completely saponifiable, but not so the neutral glycerides, containing, as they do, about 5 per cent of the glycerol-yielding radicle C_3H_2. However, as glycerol is soluble in water it does not fall under our definition of "unsaponifiable matter"; therefore, in a wider sense, the neutral fats are considered as completely saponifiable.

Most oils and fats contain in their natural state small quantities of unsaponifiable matter which consist to a great extent, in addition to other alcohols (and also to hydrocarbons), of sitosterol in the case of vegetable oils and fats, and of cholesterol in the case of animal oils and fats. Besides these two characteristic bodies some other substances occur, the nature of which has not yet been fully ascertained, such as small amounts of resinous and colouring matters. Hydrocarbons in the unsaponifiable matter of natural oils and fats have been identified in the case of chrysalis oil, cacao butter, laurel oil, and kôsam seed fat (see Vol. II. Chap. XIV.).

Waxes, notwithstanding the fact that they are hydrolysed completely on boiling with alcoholic potash, are in practice sometimes termed unsaponifiable, on account of their naturally yielding considerable quantities of "unsaponifiable" alcohols which are insoluble in water. The commercial waxes may also contain considerable proportions of free alcohols, as also hydrocarbons (see Vol. II. Chap.

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[1] *Chem. Zeit.*, 1901, 1129.

[2] Cp. *Jahrbuch der Chemie*, 1900, x. 361; cp. also Table No. 13, *Laboratory Companion to Fats and Oils Industries.* Macmillan and Co.

XIV.), which constitute "unsaponifiable matter" in the true sense of our definition.

Here we are only concerned with the isolation and quantitative determination of the unsaponifiable matter contained in, or yielded by, the natural[1] products. The further examination of the isolated unsaponifiable matter will be considered at length in Chapter IX.

Preparatory to the determination of the unsaponifiable matter, the oil or fat must be saponified as described under the heading "Saponification Value." In many cases it will therefore be found convenient to combine the determination of the saponification value with that of the unsaponifiable matter. But as the amount required for the correct determination of the unsaponifiable matter is much greater than that usually taken for the determination of the saponification value, it will depend on the quantity of material used in the saponification test, whether it is feasible to combine the two determinations. If two or three separate determinations of the saponification value have been made, then the total material will suffice for the correct determination of the unsaponifiable matter. It is not safe to employ less than 5 grms. of a substance for this test.

The unsaponifiable matter is mostly dissolved in the soap solution obtained after saponification; if somewhat larger quantities than usual are present, the unsaponifiable matter will cause turbidity of the soap solution (emulsion), or will even float on the top of it.

The separation of the unsaponifiable matter from the saponified mass is based on the ready solubility of the unsaponifiable matter in ether, petroleum ether, and other solvents, in contradistinction to the practical insolubility of the soap in these solvents, whether the soap be dissolved in water or dilute alcohol, or previously brought to the dry state. Thus, two kinds of processes suggest themselves, namely, either (1) to extract the aqueous soap solution with ether or other solvents, or (2) to treat the dried soap mass with solvents.

(1) *Extraction of the Soap Solution with Solvents*

The extraction of the unsaponifiable matter is effected by repeatedly shaking the saponified mass,[2] dissolved in a sufficient amount of water, with ether or petroleum ether, and separating the two layers by means of a separating funnel. The small quantities of soap that pass into the extract are removed by washing the ethereal solution with water. *H. Schwarz*,[3] as also *Neumann*,[4] *Fiske*,[5] *Heiduschka and Gloth*,[6] *Bacon*

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[1] "Unsaponifiable" substances are not infrequently used as denaturating agents for purposes of Custom-houses.

[2] If the mass has not been saponified completely, the unsaponified portion passes into the ether, and is weighed ultimately as so much unsaponifiable matter. Some chemists recommend, therefore, to saponify the ether extract a second time. This complication is, however, unnecessary, if the saponification be carried out with due care.

[3] *Journ. Soc. Chem. Ind.*, 1884, 649.

[4] *Berichte*, 1885 (18), 3061.

[5] *Amer. Chem. Journ.*, 1909, 510. (Illustrations, see *Journ. Soc. Chem. Ind.*, 1909, 817, and *Chem. Zeit.*, 1910, 1366.)

[6] *Pharm. Zentralh.*, 1907, No. 17.

and Dunbar[1] designed special extraction apparatus, but its employment for the purposes of fat analysis cannot be recommended.

Regarding the choice of the solvent, it is always *safer* to use common ether than petroleum ether, notwithstanding the fact that the former extracts in most cases larger quantities of soap than the latter. Thus *Lewkowitsch*[2] found in the case of shark liver oil and some kinds of whale oil that petroleum ether gave very capricious results, which were all far too low, owing, no doubt, to the "unsaponifiable matter" (cholesterol) in these oils being very sparingly soluble in petroleum ether,[3] whereas constant results were obtained when common ether was used. Due attention must be paid to the fact that the solubility of soaps in ether and petroleum ether is increased by the presence of wax alcohols and hydrocarbons; in accurate analysis it is therefore necessary, after evaporating off the solvent, to shake the extracted unsaponifiable mass with a little warm water, and to extract again with ether or petroleum ether. *Lewkowitsch*[4] recommends to incinerate the extract; a residue giving an alkaline reaction on treatment with a little water points to the presence of soap in the unsaponifiable matter. By titration with an acid the amount of alkali is found and the amount of soap can be calculated approximately.

If the soap solutions happen to be neutral, dilution with water will produce slight hydrolysis of the soaps and "acid soaps" (such as sodium bistearate, see Chap. III. p. 128) are formed. Such soaps are somewhat soluble in ether; it is therefore advisable, when using ether, to render the soap solutions strongly alkaline by adding an excess of alkali. Petroleum ether, on the other hand, more readily dissolves alkaline soaps, whereas neutral soaps are almost insoluble in this menstruum.

Very often a distinct separation into two well-defined layers does not take place readily, and emulsions are formed on shaking which require a very long time to separate, if, indeed, they separate at all. The last eventuality occurs in the case of waxes and notably so in the case of wool wax. In such cases, if ether has been used for extraction, it will be found most convenient to add a little alcohol or glycerin after shaking, and to impart a slight rotary movement to the separating funnel without, however, agitating. In other cases addition of a little caustic soda will more readily produce the desired effect. If petroleum ether has been employed, the formation of emulsions is best avoided by adding to the alcoholic soap solution (obtained on saponification) not more than an equal volume of water.

Sometimes a flocculent layer will appear between the aqueous solution and the solvent. In the case of wool wax *Lewkowitsch*[5] showed that these flocks consist of a soap insoluble in cold water and formed from fatty acids having a high molecular weight. The appearance of this flocculent stratum, however, does not interfere with the correct estimation of the unsaponifiable matter.

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[1] *Journ. Ind. Chem. Eng.*, 1911, 930.

[2] *Journ. Soc. Chem. Ind.*, 1896, 14; cp. also Dunlop, *ibid.*, 1908, 63.

[3] Shukoff and Schestakoff (*Journ. Soc. Chem. Ind.*, 1898, 805, 878), confirm this for bone fat cholesterol, which is readily extracted by common ether, but not so readily by petroleum ether, especially when the soap solution contains alcohol. Cp. also G. Meyer, *Chem. Zeit.*, 1907, 423.

[4] *Journ. Soc. Chem. Ind.*, 1892, 139; 1896, 14.

[5] *Ibid.*, 1892, 136.

The petroleum ether used for extraction should not contain any hydrocarbons boiling above 80° C.; otherwise it will be found almost impossible to remove the last portions of the solvent without seriously vitiating the results. The commercial article sold as boiling below 170° F. should not be taken on trust. It is therefore imperative to fractionate the petroleum ether, using a good dephlegmating column, *e.g. Young's*, and to discard any fractions boiling above 80° C. or even above 60° C. (cp. p. 282). The commercial production of "petrol" and "white spirit" has greatly increased the facilities for obtaining suitable petroleum ether.

Considering the importance of the subject, I think it best to describe fully several methods for the estimation of the unsaponifiable matter, for the reliability of which I can speak from practical experience. On the whole, preference should be given to the first method, originally proposed by *Allen and Thomson*,[1] which I describe in an amplified form as regards details. I also replace the caustic soda, recommended by *Allen and Thomson*, by caustic potash.

Saponify 5 grms. of the sample with 25 c.c. of double normal alcoholic potash in a flask under a reflux condenser, and evaporate off the bulk of the alcohol. The residual soap is dissolved in 50 c.c. of hot water, and transferred to a separating funnel of about 200 c.c. capacity, using about 20 to 30 c.c. of water for rinsing the flask. After cooling, add 30 to 50 c.c. of ether and shake the solution thoroughly. Addition of a little alcohol will accelerate the separation. The soap solution is then run off into another separating funnel and again exhausted with fresh ether. As a rule two extractions will suffice; it is, however, safer to extract a third time. The ethereal solutions are united, washed with a small quantity of water to free them from any dissolved soap, and transferred to a tared flask. The ether is distilled off on the waterbath, and the residue dried at 100° C. and weighed.[2]

Morawski and Demski[3] treat 10 grms. of the sample with 50 c.c. of alcohol and 5 grms. of caustic potash previously dissolved in a small quantity of water. The flask in which the fat is saponified is connected with an inverted condenser, and after half an hour's boiling 50 c.c. of water are added, and the mass allowed to cool. It is then transferred to a separating funnel and shaken out with petroleum ether. When the two layers have separated, the aqueous layer is drawn off as completely as possible, and the petroleum ether repeatedly washed with water, without, however, uniting the washings with the main soap solution. Instead of running the ethereal solution directly into the tared flask, it is first drawn off into another dry flask (or better into a second separating funnel; *Lewkowitsch*), and from this poured into the tared flask, so as to leave the water behind. The main soap solution is again extracted (and if need be a third time), in the same manner, and the petroleum ether added to the first portion. On distilling off the petroleum ether, the unsaponifiable matter will be left behind.

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[1] *Chem. News*, 1881 (43), 267.

[2] In the case of bone fat, Shukoff and Schestakoff do not wash the ethereal solution, but evaporate down to dryness, neutralise the extract (containing presumably acid soaps) with standard alkali, phenolphthalein being the indicator, and exhaust again with petroleum ether (see Vol. II. "Bone Fat").

[3] *Dingl. Polyt. Journ.* 258, 39.

Spitz and Hönig[1] recommend washing the petroleum ether layer with 50 per cent alcohol instead of water, thus shortening the time required for the separation of the two layers. The adoption of this suggestion will in many cases prevent the formation of troublesome emulsions.

(2) *Extraction of the Dried Soap with Solvents*

For the extraction of dry soap, ether cannot be recommended, as larger quantities of soap would be dissolved than is the case in the foregoing processes. Therefore petroleum ether, chloroform, or carbon tetrachloride are preferable.

Ten grms. of the sample are saponified, in a porcelain dish of 5 inches diameter, with 50 c.c. of an 8 per cent alcoholic caustic potash (*Allen* used soda) solution, by gently boiling on the water-bath with constant stirring until the soap commences to froth; 15 c.c. of alcohol are then added, and the boiling continued until the soap is dissolved. Next 5 grms. of sodium bicarbonate are stirred into the mass, and 50-70 grms. of freshly ignited pure sand mixed with it. After drying for twenty minutes in a water-oven, the mass is transferred to a *Soxhlet* apparatus, and extracted with petroleum ether, completely volatile below 80° or 60° C. The petroleum ether is then distilled off and the residue weighed.

In case considerable quantities of mineral oils are admixed with fatty oils, *Finkener*[2] uses the following process, which is but a slight modification of that proposed by *Allen and Thomson*: Heat 10 grms. of the sample on a water-bath with 50 c.c. of a nearly normal alcoholic solution of caustic soda, add 5 grms. of dry sodium bicarbonate to convert the excess of caustic soda into carbonate, and heat on the water-bath until the alcohol has been driven off. Transfer the hot mass to a stoppered cylinder, allow to cool, and shake thoroughly with 300 c.c. of petroleum ether. Filter into a dry flask, distil off the bulk of the petroleum ether, pour the solution on to a watch-glass, and weigh after evaporating off the remainder of the petroleum ether.

For the more complete extraction of the unsaponifiable matter from dry soap, *Ritter*[3] recommends to mix the soap with common salt previous to extraction with *ether*. The advantage of adding salt does not lie in that it offers a larger surface; hence salt cannot be replaced by sand or paper. Evidently the salt acts not only as a dehydrating agent, thus preventing the soap from passing into the ethereal solution, but it also inhibits the formation of emulsions which is apt to occlude unsaponifiable matter.[1]

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[1] *Journ. Soc. Chem. Ind.*, 1891, 1039.

[2] *Ibid.*, 1886, 457.

[3] *Chem. Zeit.*, 1901, 872.

The methods described under (1) cannot be employed for the determination of alcohols and other "unsaponifiable" portions of beeswax,[2] carnaüba wax, and other solid waxes, since not only are their alcohols sparingly soluble in the cold solvents, but the alkali soaps of the fatty acids are not readily soluble in water nor even in dilute alcohol. In these cases middle layers of flocculent matter are apt to be formed, which consist of soaps of fatty acids of high molecular weight in intimate intermixture with "unsaponifiable matter." These middle layers so persistently retain the alcohols, etc., that even frequent shaking out with solvents fails to extract their total amount. In such cases it is best to prepare insoluble soaps of the fatty acids by neutralising the saponified mass with acetic acid, using phenolphthalein as an indicator, and precipitating with calcium chloride[3] or barium chloride. The precipitate is washed, dried, mixed with sand, and boiled out repeatedly with petroleum ether.

In the case of shark liver oil and some kinds of whale oil, examined by *Lewkowitsch*,[4] very considerable quantities of soap were dissolved together with the unsaponifiable matter, so that petroleum ether is useless in these cases. For these substances one of the processes described under (1) must therefore be used.

As the amount of unsaponifiable matter in natural oils and fats depends to a considerable extent on the mode of preparation and extraction of oils and fats, the proportion varies, of course, with different specimens of one and the same oil. No useful purpose would be served by tabulating the proportions of unsaponifiable matter in the natural products. A considerable number of data ascertained in the case of commercial samples will be found in the monographs given in Vol. II. Chap. XIV.

In the case of waxes also the amount of unsaponifiable matter varies. It should be borne in mind that the greater part of the "unsaponifiable" consists of the alcoholic portion of the esters, which are accompanied by smaller amounts of hydrocarbons.

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[1] For a modification of Ritter's method for determining the proportion of cholesterol cp. H. J. Cooper, *Journ. Biol. Chem.*, 1912 (11), 37 ; (12), 197.

[2] Cp. Buchner, *Chem. Zeit.*, 1907, 570.

[3] The magnesium, calcium, strontium, barium, aluminium, zinc, cadmium, and copper soaps are soluble in both common ether and petroleum ether to a notable extent (cp. Vol. III. Chap. XV.). The least soluble are the calcium salts. Chatelan and Spiess patent a process for extracting lime salts, containing an excess of lime, or hydrosilicate and other inert substances (German patent 194,871).

[4] *Journ. Soc. Chem. Ind.*, 1896, 14.

CHAPTER VII

CHEMICAL METHODS OF EXAMINING OILS, FATS, AND WAXES—QUALITATIVE TESTS

The meaning of some of the qualitative tests which form the subject of this chapter has been pointed out already in the introduction of the preceding chapter (p. 378), and their bearing on the examination of oils, fats, and waxes has been explained in general. The prominence given formerly to some of them (such as the elaïdin test and the *Maumené* test), notably for classifying purposes, has greatly diminished within the last decades. They are described here, side by side with the other more important tests, as they are still employed by a number of chemists.

These tests comprise the following :—

(1) Elaïdin Test.
(2) Sulphur Chloride Test.
(3) Oxygen and Ozone Absorption Test.
(4) Bromide Test.
(5) Thermal Reactions.

Colour tests, which are caused by foreign matters dissolved by the oils in the course of their preparation (*e.g.* small quantities of resins, etc.), do not give, as a rule, such decisive results as do the qualitative tests just enumerated ; this is also due to a great extent to the fact that the quantity and sometimes also the nature of those impurities varies considerably in different specimens of the same kind of oil owing to the difference of the processes adopted in their commercial preparation and purification. Only in some special cases, which will be considered under

(6) Colour Tests,

do the colour reactions furnish definite indications.

1. Elaïdin Test

This test is based on the fact that olein is converted into the solid isomeric elaïdin by nitrous acid, whilst the glycerides of linolic, linolenic, and clupanodonic acids remain liquid under the same conditions. The non-drying oils yield therefore solid masses, whereas the semi-drying and the drying oils give more or less liquid products. (Cp. Chap. I. p. 62.)

The fact that fuming nitric acid has the property of thickening olive and almond oils appears to have been observed first by *Boyle* in 1661. *Poutet* in 1819 proposed this test for the examination of adulterated olive oil. *Poutet's* test, as practised in the Paris Municipal Laboratory,[1] is carried out in the following manner: 10 grms. of the oil under examination, 5 grms. of nitric acid of specific gravity 1·38 to 1·41, and 1 grm. of mercury, are placed in a test-tube, and the mercury is dissolved by shaking continuously for three minutes. The mixture is then allowed to stand for twenty minutes, when it is shaken again for one minute. The behaviour of different oils after that time is recorded in the following table:—

Kind of Oil.	Consistence.
Olive oil	Solidified after 60 minutes.
Arachis oil	,, ,, 80 ,,
Sheep's foot oil	,, ,, 120 ,,
Sesamé oil	,, ,, 185 ,,
Colza oil	,, ,, 185 ,,
Linseed oil	Forms a red, dough-like scum.
Cod liver oil	Becomes doughy, red, and forms a scum.
Whale oil	Same appearance.
Hemp seed oil	Remains unchanged.

Copper may be substituted for mercury. 10 c.c. of oil are placed together with 10 c.c. of 25 per cent nitric acid and 1 grm. of copper wire in a test-tube, and allowed to stand. *Finkener*[2] recommends for 10 c.c. of oil 0·2 grm. of copper and 0·5 grm. of nitric acid of spec. gravity 1·2.

The various modifications of the elaïdin test proposed by a number of observers have been discussed by *Archbutt*,[3] who thoroughly examined them. His results point to the following conclusions:—

(1) The test must be made at a temperature not below 25° C., and the temperature must be uniform throughout the experiment.

(2) The length of time required for solidification is of far greater importance than the ultimate consistence of the elaïdin formed.

Archbutt prepares and applies *Poutet's* reagent in the following manner: 18 grms. of mercury are placed in a dry stoppered 50 c.c. cylinder, and 15·6 c.c. of nitric acid, specific gravity 1·42, are added from a burette. The nitrous acid is entirely absorbed with production of a green colouration; as long as the reagent retains its green colour, it is fit for use. 8 grms. of the reagent are shaken up with 96 grms. of the oil in a wide-mouthed stoppered bottle, placed in water at the required temperature, and again shaken at intervals of ten minutes during two hours.

When tested in this manner, the more important oils may be arranged, according to *Allen*,[4] in four groups:—

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[1] Cp. Pelouze and Boudet, *Annal. d. Chim. et Phys.*, 1838 (69), 44.

[2] *Zeits. f. analyt. Chem.*, 1888 (27), 534.

[3] *Journ. Soc. Chem. Ind.*, 1886, 304.

[4] *Commercial Organic Analysis*, ii. 58.

(*a*) *A solid, hard mass* is yielded by: Olive oil, almond oil, arachis oil, lard oil, sperm oil, and sometimes neat's foot oil.
(*b*) *A butter-like mass* is yielded by: Neat's foot oil, Arctic sperm oil, mustard seed oil, and sometimes by arachis, sperm, and rape oils.
(*c*) *A pasty or buttery mass, separating from a fluid portion*, is yielded by: Sunflower oil, niger seed oil, cotton seed oil, sesamé oil, rape oil, cod liver oil, seal oil, whale oil, and porpoise oil.
(*d*) *Liquid products* are yielded by: Linseed oil, hemp seed oil, and walnut oil.

Archbutt experimented also with a reagent prepared by passing dry sulphur dioxide into cold nitric acid of specific gravity 1·42. This reagent thickens cotton seed oil and rape oil. The product yielded by pure cotton seed oil is red, that given by rape oil deep red.

Ten per cent of either oil if admixed with olive oil does not sensibly colour the white elaïdin yielded by the latter oil.

The hardest elaïdins are obtained from arachis oil, olive oil, and lard oil.

The elaïdin test has been specially applied to the examination of olive oil. It cannot, however, be made to serve as a quantitative reaction.[1] It has been shown first by *Hübl* that the most serious errors may be committed, when an attempt is made to draw conclusions as to the composition of an oil from differences in the time required for the formation of elaïdin, and from observations of the consistence and colour of the solidified mass, since the mode of preparing the nitrous acid, the mode of mixing the acid and oil, the shape of the vessel, and chiefly the temperature, influence the results to a very considerable extent.[2] Nor should it be forgotten that the age of an oil and the manner in which it has been kept (exposure to air and light) have an important bearing on the results of the elaïdin test. Thus *Gintl* has shown that an olive oil after exposure to sunlight for a fortnight did not yield any elaïdin at all. The results obtained in the elaïdin test are in every respect much less valuable than those furnished by the iodine test. Nevertheless the elaïdin test is still used, notably in France, in the examination of olive oils. In the comparative examination of almond oil and its congeners this test may afford some little information of a discriminative nature.

In order to obtain trustworthy results, it is indispensable to institute side by side with the oil under examination, under exactly the same conditions, comparative tests with standard oils of known purity.

2. Sulphur Chloride Test

E. Bruce Warren stated that *drying oils*, on treatment with sulphur chloride, S_2Cl_2, yield solid masses, insoluble in carbon bisulphide, whereas *non-drying oils* under the same treatment give soluble products. He based on this reaction a means of discriminating between drying and non-drying oils. The amount of drying oils in mixtures of fatty oils is determined in the following manner :—

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[1] Cp. "Oleic Acid," p. 181.

[2] The same conclusions have been restated by Welleman, *Journ. Soc. Chem. Ind.*, 1891, 800.

The reagent employed is sulphur chloride, diluted with an equal volume of carbon bisulphide. The sulphur chloride is obtained from the commercial yellow sulphur chloride ("chloride of sulphur") by fractional distillation, the portion boiling below 137° C. being rejected. (The portions having a lower boiling point may be digested with a moderate excess of sulphur and again fractionated.) The reagent, prepared as indicated, is kept in bottles closed by corks coated with paraffin wax. The exact quantity required for a test is withdrawn by means of a pipette. To perform a test, 5 grms. of the oil under examination are mixed with 2 c.c. of the reagent and 2 c.c. of carbon bisulphide in a porcelain crucible of about 120 c.c. capacity, and warmed on the water-bath, with constant stirring, until the reaction sets in. The mass soon becomes hard. The product must be broken up with a glass rod as completely as possible, in order to allow thorough expulsion of the volatile substances; it is then dried until constant weight is obtained. The appearance of the product, both before and after drying—especially with regard to colour and consistence—should be noted. The dried mass is finely powdered and exhausted with carbon bisulphide, the solution evaporated to dryness, and the residue weighed. The quantity of the insoluble portion is found by difference. (It should be noted that every trace of moisture must be rigorously excluded.)

Warren obtained the following figures with poppy seed and linseed oils :—

5 grms. of	Solid Insoluble Product.	Liquid Soluble Product.
	Grms.	Grms.
Poppy seed oil gave .	6·46	1.96
Linseed oil ,, .	6·36	0·78

Warren's method is based on older observations made by *Rochleder*,[1] *Roussin*,[2] *Perra*,[3] and *Mercier*.[4] His results, however, do not agree with *Rochleder's* statement that olive oil, pre-eminently a *non-drying oil*, yields an insoluble product; they are further contradicted by *Sommer*[5] and by *Henriques*.[6] The experiments carried out by the latter prove conclusively that no relationship exists between the drying power of an oil and the proportion of sulphur chloride required to form a solid product.

Experiments undertaken by the author (with a view to converting the sulphur chloride test into a quantitative reaction) prove the unreliability of *Warren's* statements, as will be seen from an examination of the following numbers :—

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[1] *Dingl. Polyt. Journ.* 111, 159.

[2] *Ibid.* 151, 136.

[3] *Ibid.* 151, 138.

[4] *Compt. rend.* 84, 916.

[5] German patent 50,282.

[6] *Journ. Soc. Chem. Ind.*, 1894, 47.

Oils and Fats treated with S_2Cl_2 ; 5 *grms. of fat* ; 2 *c.c.* S_2Cl_2, *and* 2 *c.c.* CS_2 (*Lewkowitsch*)

A. *Products completely soluble in Carbon Bisulphide*

Class of Oil.	Kind of Oil.	Mass thickens after Minutes.
Liquid waxes	Sperm oil, No. 1	20
	Sperm oil, No. 2	45
	Arctic sperm oil, No. 1	45
	Arctic sperm oil, No. 2	55
	Arctic sperm oil, No. 3	30
Vegetable fats	Mowrah seed oil	Do not thicken.
	Palm oil	
	Palm nut oil	
	Cocoa nut oil	
Animal fats	Lard	
	Butter fat	
	Beef tallow	
	Mutton tallow	

B. *Products not completely soluble in Carbon Bisulphide*

Class of Oil.	Kind of Oil.	Solidifies after Minutes.		Soluble in CS_2.
		In the Cold.	On the Water-bath.	
				Per cent.
Drying oils	Linseed	10	2	14·4
	Tung, Chinese	1½	...	...
	Hemp seed	11	...	9·2
	Poppy seed	21	...	10·6
Fish oils	Japan fish	9	...	12·4
Liver oils	Cod liver, pure	15	...	4·4
	Cod liver, rancid	1½	...	6·4
Blubber oils	Seal	11	...	4·4
	Whale	13	...	3·0
Semi-drying oils	Cotton seed	20	4	24·0
	Sesamé	21	...	18·4
	Colza	23	...	2·8
	Rape	12	2	4·2
	Croton	18	...	25·4
Non drying oils	Peach	26	...	4·8
	Almond, sweet	27	...	4·0
	Almond, bitter	28	...	3·4
	Arachis	30	...	6·0
	Olive	22	4	4·2
	Castor	½	at once	3·8
	Sheep's foot	36	...	6·0
	Horses' foot	20	...	13·6
	Neat's foot	23	...	9·4
	Lard	10	...	15·0
	Tallow	12	...	29·8

The author further observed a remarkable difference in the action of sulphur chloride on vegetable oils on the one hand, and on their mixed fatty acids on the other. Whereas the oils are acted upon quickly with the formation of a solid product, the free acids react more slowly, yielding semi-solid, viscous products.

The chemical change which takes place, when sulphur chloride is allowed to act on oils, appears to consist in an absorption of the elements of sulphur chloride, much as iodine chloride is absorbed in *Hübl's* test. *Henriques* showed that after treatment with sulphur chloride, oils have far lower iodine absorption values than before. *Ulzer and Horn*, and afterwards *Henriques*, proved that the products of reaction contain sulphur and chlorine in approximately the same proportion as does sulphur chloride (S_2Cl_2). Thus, the action of sulphur chloride on oils appears to consist in the conversion of unsaturated fatty acids or their glycerides into saturated compounds. Further investigations must show whether a separation of saturated from unsaturated glycerides can be effected by means of this reagent. In this connection the difference between the behaviour of lard and tallow on the one hand and that of their " oleines " on the other is somewhat remarkable.

The researches of *C. O. Weber*[1] have thrown much light on the rationale of the chemical reaction involved. Further information on that subject will be given under " India-Rubber Substitutes " (Vol. III. Chap. XV.). For the thermal reaction with sulphur chloride cp. p. 488.

3. Oxygen and Ozone Absorption Tests

The absorption of oxygen from the atmosphere has a very important bearing on the liability of oils to cause spontaneous combustion when spread in a finely divided state on fibrous organic substances (cp. Vol. III. Chap. XV. " Wool Oils "). It has also very great importance in the industries of paint oils, boiled oils, and varnishes (cp. Vol. III. Chap. XV.).

It has been pointed out already (p. 416) that the iodine absorption of oils and fats stands in close relationship to their absorption of oxygen, and that the latter property, being a measure of the drying power of oils, had been used for purposes of classification. It has further been explained that the classification based on the iodine value includes the subdivision of the oils into drying, semi-drying, and non-drying oils.

Although the extremes of these groups, as represented by linseed oil and olive oil, are sharply defined, in that the former easily " dries " to a solid substance on exposure to air, even at the ordinary temperature, whereas the latter remains comparatively unchanged under the same conditions, there exist so many gradations between these two extremes, that a sharp line of demarcation cannot be drawn. The gradual transition from true drying oils to decidedly non-drying oils admits of the interposition of an intermediate class of semi-drying oils ;

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[1] *Journ. Soc. Chem. Ind.*, 1894, 11.

but as the process of drying with formation of a skin may occupy in some cases as much as several months, it is evident that a strict subdivision cannot be based on the more or less pronounced drying properties.

It should be noted that the distinction drawn here between drying, semi-drying, and non-drying oils is based on their behaviour at the ordinary temperature, for according to *Livache* all oils, even solid fats, are oxidised on exposure to air at higher temperatures (see below).

The foregoing notes may be illustrated in a general manner by some comparative tests due to *Archbutt.*[1]

Kind of Oil.	Time required for a thin film to dry in air at 50° C. 0·1 grm. oil on a glass surface 7 sq. cm.
Linseed	About 12 hours
Maize	,, 18 ,,
Cotton seed	,, 21 ,,
Curcas	,, 24-30 hours
Rape	,, 48 ,,
Olive	More than 13 days.

The chemical changes which take place while oils are "drying" are very imperfectly understood, and further experiments are required to elucidate this important question (cp. "Boiled Oil," Vol. III. Chap. XV.). The drying properties of a vegetable oil seem to stand in direct ratio to the proportion of glycerides of linolenic and linolic acids in the oil. Therefore, in a general way, the rule holds good that the higher the iodine value the better will an oil dry. (In the case of tung oil the drying power seems to reside in elæomargaric acid.) This rule satisfactorily explains the fact that even closely related oils, such as the oils of the rape oil group, behave differently when exposed to the atmosphere. In the case of animal oils of the fish, liver, and blubber oil groups, the oxygen absorption must be ascribed to the presence of clupanodonic acid.

If oils be treated with **ozone** a direct proportionality is observed between their iodine value and the amount of *ozone* absorbed. *Molinari* and his collaborators (*Soncini, Fenaroli,*[2] *and Barosi*[3]) have shown that the glycerides of unsaturated fatty acids absorb as many molecules of ozone as they contain pairs of doubly-linked carbon atoms in their molecule. The amount of ozone absorbed is found in a direct manner by dissolving the oil under examination in a suitable solvent and passing a current of ozonised air through the solution, until no further increase in weight takes place. In the earlier experiments the complete absorption required a prolonged time, but by heating the solution containing the ozonide in a vacuum on the water-bath at 60° C., constant weight can be obtained within half an hour, so that the whole determination of the increase in weight by absorption of ozone—termed "**ozone value**"—need not require more than two to three hours. The increase which a specimen of olein having the iodine value 85·8 (theory 86·2, see p. 406) gained on being saturated with ozone in a solution of (petroleum) hexane was 16·45 per cent, whilst theory required an increase of 16·27 per cent. The product so obtained has been described above as (p. 28) "Triolein (Olein) Ozonide." *Fenaroli* obtained the "ozone values" given in the following table; against the observed numbers are placed, in the last column, the theoretical "ozone values" calculated from the corresponding iodine values :—

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[1] *Journ. Soc. Chem. Ind.*, 1899, 347.

[2] *Annuario della Soc. Chimica di Milano*, 1903, ix. p. 507 ; 1905, xi. p. 80 ; 1906, xii. *fascie* i., ii., iii., and iv. ; *Berichte*, 1906, 2735 ; *Gazz. chim.*, 36, ii. 292.

[3] *Berichte*, 1908, 2789 ; 2793.

	Ozone Value found.	Ozone Value calculated from Iodine Value.	Iodine Value.
Linseed oil . .	34	33·5	176·8
Maize ,, . .	21·6	21·6	114·1
Olive ,, . .	16·0	15·9	83·8
Castor ,, . .	16·2	16·3	86·4
Cholesterol . .	24·85	[1]	65·8
Phytosterol . .	24·85	[1]	65·8

It would seem to follow from the numbers stated in the last table that the information gained by the determination of the ozone value is fully comparable with that obtained by determining the iodine value. Since, however, in practical work the determination of the iodine value is very much simpler than that of the ozone value, it is not likely that the determination of the ozone value will supplant that of the iodine value.

In the case of the absorption of **oxygen** from air no such quantitative proportionality as exists in the case of ozone has been observed hitherto. Olein absorbs six atoms of iodine, and, as shown above, assimilates a closely corresponding amount of ozone, yet it does not readily absorb oxygen from the air. In fact its fatty acid, oleic acid, which absorbs two atoms of iodine and, in conformance therewith, one molecule of ozone (see Chap. III.), possesses no drying properties. Therefore a direct proportionality between the quantities of **oxygen** and **iodine** which drying oils assimilate, cannot be established, inasmuch as two atoms of absorbed iodine should correspond to one atom of oxygen. Still, a certain proportionality does exist, as will be seen from the following table, in which the percentage of oxygen actually absorbed is compared with the quantity of oxygen calculated from the iodine absorption value by multiplying the latter by $\frac{16}{254}=0{\cdot}063$.[2]

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[1] The theoretical "ozone number" for two molecules of ozone is 24·84. Cholesterol and phytosterol absorb, however, only two atoms of bromine (or one molecule of iodochloride, as far as has been proved in the case of cholesterol; see p. 268). It should also be pointed out that according to Harries, *Liebig's Annal.* 374, 291, the ozone addition method does not always yield correct results.

[2] Cp. Engler and Weissberg, *Berichte*, 1900, 1097, and Vol. III. Chap. XV.

Kind of Oil.	Oxygen Absorption.	
	Determined by Weighing.	Calculated from Iodine Value.
	Per cent.	Per cent.
Linseed . . .	16·6-19·3[1]	10·77-12·66
Hemp seed . . .	13·4	9·324
Walnut . . .	7·9	9·135
Poppy seed . .	6·8	8·28-9·01

If a convenient method were known for the accurate determination of the *oxygen* which is absorbed during the drying process, it would be possible to class the determination of the drying power, or, as it might be termed, the "oxygen value," amongst the quantitative tests. Determinations made by earlier observers[2] were done in a very unsystematic fashion, insufficient regard having been paid to such important factors as temperature,[3] influence of light,[3] moisture of the atmosphere, thickness of layer exposed, age of the oil, etc.

The earliest experiments consisted in exposing different oils to the atmosphere, and ascertaining the increase of weight which had taken place after a certain lapse of time. The greater the gain in weight, the greater was considered to be the oxygen absorption, or, in other words, the greater the drying power of the oil. But the numbers thus obtained could give but limited information as to the oxidation which had taken place. For if an oil were exposed in dishes in a layer about one centimetre thick, as was usually the case in these earlier experiments, a skin would soon be formed on the top layer. This would prevent further access of the oxygen of the atmosphere to the oil, so that whilst the top layer might represent a completely oxidised oil, the layer immediately below would only be partly oxidised, owing to diffusion of oxygen into that middle layer, and the bottom layer would represent practically unchanged oil.[4] This can be readily ascertained by exposing linseed oil to the atmosphere, in a porcelain dish, in a layer of about one centimetre thickness. After about one week a dry skin will have formed on the top; on breaking the skin it will be found that the layer immediately below is still viscid, whilst the bottom layer is liquid. Hence, such tables as those given by *Mulder*[5] and by *Kissling*[1] are of limited value, and I therefore omit them here. Besides, no account was taken of the fact that the increase of weight (ascertained by weighing) merely represents the algebraical sum of all the changes that have occurred, and that therefore the increase of weight cannot be identified with the amount of absorbed oxygen. In the course of drying, other changes take place (such as the formation of volatile acids, as also of carbon dioxide) which cause a loss, the amount of which is obliterated by the preponderance of the gain through absorption of oxygen (cp. Vol. III. Chap. XV. "Oxidised Oils").

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[1] Weger found higher values; and Genthe, even 25·7 per cent (in ultra-violet light); see Vol. III. Chap. XV. "Boiled Oil." With regard to the action of ultra-violet light cp. also E. v. Aubel, *Compt. rend.*, 1909 (149), 983. Compare also Cooper Hewitt lamp, Vol. II. "Linseed Oil."

[2] A number of methods due to earlier observers such as Casselmann, Fox, Bach, a. o., were enumerated in the second edition of this work (1898, p. 285), but have been omitted in later editions on account of their uselessness. Recent revivals of these methods need not therefore be referred to.

[3] Cp. Genthe, *Zeits. f. angew. Chem.*, 1906, 2089, and Vol. III. Chap. XV. "Boiled Oil."

[4] Weger, *Zeits. f. angew. Chem.*, 1898, 492, 507; *Chem. Rev.*, 1898, 315.

[5] *Chemie der austrocknenden Oele.*

Since the drying of an oil requires a protracted length of time, attempts were made to accelerate the progress of drying by mixing with the oils finely divided lead (*Livache*[2]), or finely divided copper (*Hübl*; *Lippert*[3]). *Livache's* lead powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum. The test is carried out as follows: Spread about 1 grm. of lead (or copper) powder, weighed off accurately on a somewhat large watch-glass, in a thin layer, and allow to fall on to it from a pipette 0·6 to 0·7 grms. (not more) of the oil to be tested, placing each drop separately on the lead (or copper) powder, taking care that the drops do not run into one another. Then allow the watch-glass to stand at the ordinary temperature exposed to light. (The acceleration of the drying by the catalytic action of metals or their salts, will be discussed under "Driers" (Vol. III. Chap. XV.).)

In this process, linseed oil reaches the maximum absorption within a few days, whereas under ordinary conditions the same result is only arrived at after a much longer time has elapsed. *Livache* states that drying oils absorb the maximum quantity of oxygen after eighteen hours, or in some cases after three days, whereas non-drying oils do not gain in weight before the lapse of four or five days. *Weger*[4] condemns *Livache's* process, and recommends to employ larger quantities of lead, so that for 0·2 grm. of oil there should be taken at least two grms. of lead powder. But even in that case the results, as shown below, were not found to be satisfactory.

The following table reproduces a number of results obtained by *Livache's* method. There is added the gain in weight of the free fatty acids, since the free fatty acids, with the notable exception of those of cotton seed oil, behave in *Livache's* test much like their glycerides, so that their increase in weight corresponds to the gain in weight of the neutral oils.

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[1] *Journ. Soc. Chem. Ind.*, 1891, 778; 1895, 479. Cp. also second edition of this work, p. 285.
[2] *Ibid.*, 1886, 494.
[3] *Chem. Revue*, 1899, 67.
[4] *Chem. Revue*, 1898, 246.

[TABLE

Oxygen Absorption by Livache's Test

Kind of Oil.	Gain in Weight of 100 Parts:					Observer.
	Of Oil after			Until Weight remained constant (*Tortelli*[1]).	Of Fatty Acids after 8 Days.	
	2 Days.	3 Days (*Jean*[1]).	7 Days.			
Linseed . .	14·3	...	...	...	11·0	Livache
Stillingia . .	8·72	...	12·45 (8 days)	...	...	,,
Walnut . .	7·9	...	...	...	6·0	,,
Poppy seed .	6·8	...	...	...	3·7	,,
Cotton seed .	5·9	...	...	...	0·8	,,
Beech nut .	4·3	...	...	...	2·6	,,
Colza . .	0·0	...	2·9	...	2·6	,,
Rape . .	0·0	...	2·9	...	0·9	,,
Sesamé . .	0·0	...	2·4	...	2·0	,,
Arachis . .	0·0	...	1·8	...	1·3	,,
Olive . .	0·0	...	1·7	...	0·7	,,
Japan fish .	...	8·194				
Menhaden .	...	5·454				
Sardine . .	...	...	...	[illegible]·22		
Cod liver . .	...	6·383	...	5·43		
Whale . .	...	8·266	...	7·62		
Neat's foot .	...	...	...	1·19		
Sperm . .	...	1·629				

In order to effect more rapid oxidation *Bishop*,[2] following the method adopted in practice with paint oils (Vol. III. Chap. XV.), spreads the oil on precipitated silica, and adds a little manganese rosinate (see "Driers," Vol. III. Chap. XV.) obtained from the commercial product by extraction with petroleum ether or common ether. *Bishop* proceeds as follows: 5 to 10 grms. of oil are placed in a dish and mixed on the water-bath with exactly 2 per cent of manganese rosinate, until the latter is completely dissolved. 1 grm. of calcined precipitated silica is weighed into a flat-bottomed dish, and 1·02 grm. of the rosinated oil is added, drop by drop, by means of a pipette. The mass is intimately mixed with the aid of a glass rod, and carefully spread over the bottom of the dish so as to offer a large surface to the air; it is then left at a temperature of 17°-25° C. in the case of drying oils, and at 20°-30° C. in the case of other oils. The dish is weighed after six hours, and twice more in the twenty-four hours, a fresh surface being exposed after each weighing by stirring the mass. The maximum increase in weight, calculated to per cent, is termed by *Bishop* the "*degree of oxidation.*"

The following table contains the results obtained by *Bishop*:—

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[1] Allowed to stand for three days in a dry atmosphere (under a desiccator over sulphuric acid).

[2] *Journ. Pharm. et Chimie*, 1896, 55; *Journ. Soc. Chem. Ind.*, 1896, 475.

Oil.	Specific Gravity.	Absorption of Oxygen in per cent "Degrees of Oxidation."	Mean Values.
Linseed oil, French	0·9327	17·70-16·40 [1]	17·05
,, ,, River Plata . . .	0·9304	15·45-15·00	15·20
Hemp seed oil	0·9287	14·55-14·30	14·40
Poppy seed oil, French . . .	0·924	14·50-13·90	14·20
Walnut oil, French	0·924	13·70	13·70
Cotton seed oil	0·924	8·60	8·60
,, ,, freed from stearine .	0·923	9·60-9·30	9·45
Sesamé oil, Senegal	0·9215	8·95-8·50	8·70
,, ,, Indian	0·921	7·40	7·40
Arachis oil, African	0·916	6·70	6·70
,, ,, white	0·916	6·50	6·50
Colza oil, French	0·9142	6·40 (?)	6·40 (?)
,, ,, Indian	0·9137	5·90-5·80 (?)	5·85 (?)
Olive oil	0·9155	5·30 (?)	5·30 (?)

Fahrion [2] proposed to determine the oxygen absorption of an oil by impregnating with it a strip of chamois leather, and exposing it, suspended from a brass hook, to the atmosphere. Side by side with it he suspended a similar strip of leather, serving as a blank test, so as to eliminate the influence of evaporation of moisture from the leather, etc.

Fahrion's results are tabulated below; the absorption of oxygen has been calculated to 100 parts of oil used :—

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[1] Lippert, *Journ. Soc. Chem. Ind.*, 1898, 588, found in some cases, when using comparatively fresh oils, the absorption from 17 to 18 per cent, and in a few cases even 19 per cent; but he never obtained 20 per cent.

[2] *Journ. Soc. Chem. Ind.*, 1895, 811.

[TABLE

	Iodine Value.	Absorption of Oxygen by 100 parts of Oil after														Maximum.	Absorption according to Livache.	Calculated from the Iodine Value. I×0·063.
		1 Day.	2 Days.	3 Days.	4 Days.	5 Days.	6 Days.	7 Days	8 Days.	9 Days.	10 Days.	14 Days.	21 Days.	28 Days.	56 Days.			
Blank test .	..	0·0	1·0	1·3	0·9	1·4	−0·6	1·3	0·0	0·5	1·8	−0·5	1·1	3·3	−2·5	..	..	..
Olive oil . .	82·1	0·2	1·0	1·2	0·9	1·4	−0·4	1·1	−0·1	0·5	1·7	−0·5	0·7	3·5	−2·5	0·2	1·7	5·2
Sesamé oil .	110·2	0·1	1·2	0·9	0·5	1·1	−0·5	1·0	0·0	0·7	2·0	1·1	4·7	6·6	−0·5	3·6	2·4	7·0
Rape oil . .	102·4	0·1	1·1	1·3	1·0	1·8	0·5	2·5	2·0	2·8	4·6	2·3	3·2	6·3	−0·2	2·8	2·9	6·5
Cotton seed oil	109·2	−0·1	0·8	1·4	1·2	3·1	2·2	5·0	4·7	5·7	7·4	2·5	1·6	5·2	−1·4	5·6	5·9	6·9
Poppy seed oil	135·9	0·3	2·0	3·2	4·3	7·1	7·3	9·7	7·0	7·3	8·0	3·3	2·7	6·7	−0·3	8·4	6·8	8·6
Walnut oil .	149·2	−0·2	2·0	4·4	7·1	9·7	8·4	9·6	7·2	7·3	8·3	4·0	4·2	8·4	−1·3	9·0	7·9	9·4
Linseed oil .	175·8	0·1	1·5	2·0	3·8	12·3	11·8	13·2	10·4	11·3	11·8	7·9	8·2	12·6	4·5	12·4	14·3	11·1
Cod liver oil .	171·0	−0·6	1·1	8·1	10·0	10·9	8·0	10·4	8·0	8·5	10·1	6·3	6·3	11·8	4·3	9·5	6·4	10·8

A modification of this method, using cotton yarn as a substratum (*Fahrion*[1]) applied to the isolated fatty acids, will be described below (Chap. VIII. p. 567).

From the foregoing notes it will be gathered that the changes which accompany the drying of an oil are of a very complicated nature, and depend on a variety of factors, namely, the age of an oil, the action of oxygen through exposure to air previous to examination, length of time of exposure, thickness of layer, atmospheric conditions,[2] temperature, and influence of light. Investigations as to the influence which each of these factors exercises to the exclusion of the others are obviously beset with great difficulties, and have not been carried out hitherto in a systematic fashion.

The influence which the length of time during which an oil is exposed has on the determination of the drying power is illustrated by the following table :—

No. of Oil.	Weight of Oil. Grms.	Weight of Lead. Grms.	Gain in Weight of 100 Parts after			
			1 Day.	3 Days.	6 Days.	9 Days.
1	3·246	1·012	14·4	15·7	unchanged	...
2	3·154	0·653	2·45	12·0	15·9	unchanged

No. 1 must be considered the better drying oil, although both oils finally absorb the same amount of oxygen.

Regarding the influence of temperature, it has been established so far that at elevated temperatures the absorption of oxygen takes place at an increased ratio.

Livache showed that rape oil and olive oil, when kept at a sufficiently high temperature (120°-160° C. with or without previous treatment with litharge or manganese borate), behave like drying oils and become finally transformed into a solid substance, viz. *Mulder's* "linoxyn" (see Vol. III. Chap. XV.). Further experiments of *Livache* prove that all fatty substances without exception, whether of vegetable or animal origin, even solid animal fats, can be converted into "linoxyn," the rapidity of the change depending on the temperature used and on the previous treatment to which the fatty substance has been subjected.[3]

Lippert, as also *Weger*, undertook a systematic study of the drying power of oils, by exposing them to the action of the atmosphere in very thin layers on glass plates. It was found that glass could not be replaced by any other materials lighter in weight; thus celluloid, gelatin, and even ebonite were found completely useless. Sheets of mica, although useful for the work, are too easily damaged, and even sheets of thin

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[1] *Zeits. f. angew. Chem.*, 1910, 722; 1106.

[2] Cp. difference between boiled oil prepared with lead and manganese driers respectively (Vol. III. Chap. XV.).

[3] Cp. Fleurent, *Journ. Soc. Chem. Ind.*, 1898, 852.

metal have the drawback of being too easily creased. Necessary precautions in this test are: that the glass be perfectly clean, free from dust, and that the oil be spread with the greatest possible care in an evenly thin layer. If the layer is of uneven thickness, increase of weight may occur at one place, whilst simultaneously in a thinner layer loss of weight may take place. A series of experiments showed that the thinner the layer of oil exposed, the more rapidly is oxygen absorbed at the commencement of the experiment, but after twenty-four hours an equilibrium seems to be established. The thicker the layer the smaller is the increase, but if the layer is too thin, unreliable results will be obtained. The best conditions seemed to be reached by spreading the oil so that about 0·0005 grm. covered one square centimetre of a glass plate.

The table facing this page reproduces the results collated from *Weger's* table.

It will be seen that the process is an extremely tedious one, and depends on the accuracy with which a few decimilligrams can be ascertained. Besides, the method does not yield absolute figures, and can only be used as a guide in comparative tests. It must, therefore, depend on the given circumstances whether this process should be applied. For if it is merely a question of discriminating between drying, semi-drying, and non-drying oils, the iodine value will not only be the most convenient sorting test, but will at the same time furnish quantitative results, as explained already. It should be noted, however, that the iodine value must not be accepted as tantamount to a measure of the drying power. To take a striking example, fish and liver oils absorb approximately as much iodine as do the best drying oils, and yet they are greatly inferior to the latter as regards oxygen absorption power. Furthermore, fish and liver oils differ most materially from the "drying oils," in that they do not form a skin as does linseed oil.[1]

4. Bromide Test

In the course of his investigations on unsaturated fatty acids, *Hazura* studied also the action of bromine on these acids (see Chap. VIII.). *Hehner and Mitchell*[2] applied *Hazura's* suggestive methods to the glycerides themselves, and worked out a process which offers a means of differentiating qualitatively drying oils, as also fish, liver, and blubber oils, from oils belonging to the semi-drying group and from liquid waxes.

This process is best applied in the following manner, which embodies some slight modifications worked out in the author's laboratory: Dissolve 1 to 2 grms. of oil in 40 c.c. of ether, to which a few c.c. of glacial acetic acid have been added, cool the solution in a corked flask to 5° C., and add bromine from a finely-drawn out pipette,[1] drop by drop, until the brown colouration remains permanent. (If the temperature were allowed to rise, evolution of hydrobromic acid would become noticeable. In that case the experiment must be rejected.) After standing for three hours at a temperature of 5° C. the liquid is filtered through a plaited filter, and the precipitate washed four times in succession, using each time 10 c.c. of chilled ether. The residue is finally dried in a water-oven to constant weight. *Tolman* prefers to centrifuge the precipitate in a tube and wash it therein.[2]

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[1] With regard to the changes which oils suffer under the influence of atmospheric oxidation cp. H. C. Sherman and M. J. Falk, *Journ. Amer. Chem. Soc.*, 1903 [25], 711; 1905 [27], 605.

[2] *Analyst*, 1898, 313.

The following are the theoretical numbers of brominated triglycerides, the fatty acids of which contain eighteen atoms of carbon :—

	Formula.	Bromine. Per cent.
Octobrominated stearin, Octobromoclupanodonin	$C_3H_5(C_{18}H_{27}O_2Br_8)_3$	68·92
Hexabrominated stearin, Hexabromolinolenin .	$C_3H_5(C_{18}H_{29}O_2Br_6)_3$	62·28
Tetrabrominated stearin, Tetrabromolinolin .	$C_3H_5(C_{18}H_{31}O_2Br_4)_3$	52·23
Dibrominated stearin, Dibromoölein . . .	$C_3H_5(C_{18}H_{33}O_2Br_2)_3$	35·19

The hexabrominated compounds obtained from linseed oil melt at about 140° C. and decompose at about 155° C., the octobrominated compounds do not melt below 200° C. and blacken above that temperature.

In order to illustrate the usefulness of this method, the author may point to the fact that tung oil was found in his laboratory[3] to yield no hexabromides, whereas *Maquenne's* formula $C_{18}H_{30}O_2$ for the chief unsaturated fatty acid in tung oil postulated that hexabromides should be obtained. This apparent discrepancy has been satisfactorily explained by *Kametaka*,[4] who established the formula of $C_{18}H_{32}O_2$ for elæomargaric acid.

Halphen slightly modified *Hehner and Mitchell's* method by employing the following brominating reagent: 28 volumes of glacial acetic acid, 4 vols. of nitrobenzene, and 1 vol. of bromine. *Halphen* mixes 0·5 c.c. of the sample with 10 c.c. of the reagent in a test-tube, and is thus enabled to differentiate qualitatively between (1) oils which give no precipitate even after one hour's standing and form a clear solution ; (2) those which give no precipitate after one hour's standing, but furnish a slightly turbid solution ; (3) those which become distinctly turbid and yield a precipitate ; and (4) oils which become turbid and separate into two layers on standing. In this form the test yields no more definite information than the iodine absorption test (cp. also Vol. II. Chap. XIV. " Marine Animal Oils ").

It is therefore far better to carry out the test in its quantitative form as described above. The following table states the amounts of the bromo-compounds of glycerides obtained from a number of oils.

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[1] Cp. also Chap. VIII.

[2] *Journ. Ind. Eng. Chem.*, 1909, 342.

[3] *Analyst*, 1902, 237.

[4] *Journ. Chem. Soc.*, 1903, 1042.

The numbers, due to *Walker and Warburton*, and to *Stadler*,[1] were determined in the author's laboratory.

Kind of Oil.	Yield of Insoluble Bromides from Glycerides. Per cent.	Observer.
Perilla	53·6	Lewkowitsch
Linseed (iod. val. 181) . . .	23·14 ; 23·52	Walker and Warburton
„ (iod. val. 186·4) . .	24·17	Lewkowitsch
„ (iod. val. 190·4) . .	37·72	„
Linseed	23·86-25·8	Hehner and Mitchell
Linseed, Baltic (iod. val. 197) .	47·5 ; 48·1	Ingle
„ Indian (iod. val. 185) .	39·1 ; 39·3	„
„ Dutch (iod. val. 181·5) .	36·9	„
„ Argentine (iod. val. 179·5)	35·3 ; 33·7	„
Tung, Chinese	nil	Hehner and Mitchell
„ 1st sample	nil	Walker and Warburton
„ 2nd sample	0·38 ; 0·39	„
Candle nut	8·21 ; 7·28	„
Hempseed	8·82	Sprinkmeyer and Diedrichs
Walnut	1·42-1·9	Hehner and Mitchell
Walnut	2·22	Sprinkmeyer and Diedrichs[2]
Safflower	0·65-1·65	Walker and Warburton
Soya bean	3·73[3]	Lewkowitsch
„	3·62	Sprinkmeyer and Diedrichs[2]
Poppy seed	nil	Hehner and Mitchell
Maize	nil	„
Cotton seed	nil	„
Cotton seed[4]	nil	Lewkowitsch
Sesamé	0·06-0·16	Sprinkmeyer and Diedrichs[2]
Rape	0·73	Stadler[5]
Brazil nut	nil	Hehner and Mitchell
Almond	nil	„
Olive	nil	„
Japan fish	21·14 ; 22·07	Walker and Warburton
Fish, deodorised	49·01 ; 52·28	„
Menhaden	61·8	Ingle
Cod liver	42·9	Hehner and Mitchell
„	35·33 ; 33·76	Walker and Warburton
Cod, Newfoundland . . .	32·68 ; 30·62	„
Shark liver	22	Hehner and Mitchell
„ „	21·22 ; 19·08	Walker and Warburton
Seal	27·54 ; 27·92	„
Whale	25	Hehner and Mitchell
„ old sample	15·54 ; 16·14	Walker and Warburton
„ fresh sample . . .	20·1-22·6	Lewkowitsch
Sperm	2·61 ; 2·42	Walker and Warburton
„	3·72 ; 3·69 (after standing 48 hours)	„

The brominated glycerides do not crystallise well and offer difficulties in filtration. Especially is this the case with the octobrominated glycerides. The quantitative results obtained by the several observers vary considerably; this is due to variations of the conditions under which the determinations were made, such as temperature, concentration, time of standing.

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[1] *Analyst*, 1902, 237.

[2] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1912, xxiii., 684.

[3] Melting point 148° C.

[4] Cooled.

[5] Determined in the author's laboratory.

In the author's opinion, derived from very extensive practice with this method, it is therefore preferable to apply the bromide test to the fatty acids (cp. Chapter VIII.), isolated with due care so as to avoid oxidation by the oxygen of the air (cp. Chap. III. p. 110).

5. Thermal Tests

(*a*) *Thermal Reaction with Sulphuric Acid*: *Maumené Test*

Maumené,[1] investigating systematically the reaction first observed by *Achard* (in 1777), ascertained that, on mixing concentrated sulphuric acid with drying oils, a higher temperature was produced than is the case with non-drying oils; *Maumené* then proposed the *sulphuric acid test* as a useful reaction in the examination of fats.

Fehling, *Casselmann*, *Allen*, *Archbutt*, and others confirmed *Maumené's* observation, and proved that comparable results may be obtained, if the experiments are carried out under exactly the same conditions. It is therefore necessary to use *always* sulphuric acid of precisely the same strength (the acid must be kept carefully protected from access of air), to cool the oil and the reagent to exactly the same temperature before commencing the operation, and even to use the same vessel for each determination.[2] (*Archbutt*, however, is of the opinion that it is unnecessary to work at some constant initial temperature.)

Maumené[3] found that sulphuric acid heated to 320° C., and used immediately after cooling, gave a different temperature reaction from that shown by an acid that had not been so treated. This is due to the partial dissociation of the sulphuric acid which takes place on heating. Since, according to *Lunge and Naef*, sulphuric acid of 99 per cent of SO_4H_2 has the same specific gravity as 96 per cent acid, it is best to ascertain the strength of the sulphuric acid by titration (*Archbutt*[4]).

The influence of the concentration of the acid on the result is shown in the following table due to *Archbutt* (cp. also below, *Thomson and Ballantyne's* table, p. 485):—

Kind of Oil.	Rise of Temperature observed with Acid containing per cent of SO_4H_2:						
	97·38.	96·71.	95·72.	94·72.	93·75.	92·73.	91·85.
	°C.	°C.	°C.	°C.	°C.	°C.	°C.
Olive	43·25 42·25	42	39	36·5	34·5	31	28 29·25
Rape	63 ; 62	61	58	54	50·25	47	40·5 ; 43
Olive, impure	48·5 48·5	47 ; 47·5	43·75 44·25	40·75 40·25	38·5 ; 39	35·5 35·5	32·5 32·5

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[1] *Compt. rend.*, 1882 (95), 572.

[2] *Journ. Soc. Chem. Ind.*, 1891, 234.

[3] *Compt. rend.* 92, 721.

[4] *Journ. Soc. Chem. Ind.*, 1886, 304.

It should also be noted that on using a somewhat weak acid the rise of temperature is very slow.

Archbutt recommends the following method of operating: 50 grms. of the oil (weighed accurately to within 10 to 20 milligrams) are placed in a beaker of 200 c.c. capacity. The bottle of acid and the beaker of oil are then placed in a large vessel of water until both liquids have acquired the same temperature, viz. about 20° C. The beaker containing the oil is removed, wiped outside, and placed in a " nest " of cardboard, having hollow sides stuffed with cotton wool, or in a larger beaker lined with cotton wadding. A thermometer is then immersed in the oil, and after the temperature has been read off, 10 c.c. of the concentrated sulphuric acid are rapidly withdrawn from the bottle with a pipette and run into the oil; the time allowed for the emptying of the pipette should occupy only one minute. During this time the oil should be stirred with the thermometer, and the stirring continued until no further rise of temperature is observed. The highest point is easily noticed, as the temperature remains constant for some little time before it begins to fall.

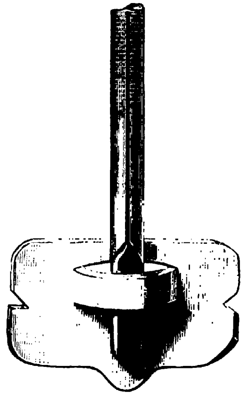

Fig. 39.

In order to secure a more perfect intermixture of oil and acid, *Allen* fastens the thermometer to a tin plate, bent into the shape of a screw-paddle. This piece of apparatus, shown in Fig. 39, forms an efficient stirrer, producing a complete intermixture of the two liquids.

The numbers of the following table, expressing the rise of temperature by *Maumené's* test for various oils, are arranged in the order of the magnitude of the iodine values, so as to show the correlation (if any) of the thermal reaction and the iodine values of the oils. The results are mean numbers obtained by different observers who worked under different conditions. Therefore the individual numbers given under the heading of each oil and fat in Vol. II. Chap. XIV. should also be consulted.

Oil.	Class.	Group.	Maumené Test. °C.	
Perilla	Drying oils		127[1]	
Linseed			110-126	
Stillingia			136·5	
Cedar nut			98	
Garden rocket			126	
Hemp seed			97	
Walnut, Nut			101-103	
Safflower			120	
Soya bean			88[2]; 91·2[1]	
Poppy seed			88	
Millet seed			67·5	
Niger seed			81·5	
Sunflower			72	
Fir seed			98·5	
Pine nut			71	
Madia			97	
Tobacco seed			100	
Isano			115	
Mohamba			55	
Cameline	Semi-drying oils	Cotton seed oil group	82-117	
Grape seed			53-82	
Maize [corn]			81-86	
Beech nut			64	
Kapok			95	
Cotton seed			75-90	
Sesamé			65·5	
Myrtle seed			39 (?)	
Zachun			75·5	
Brazil nut			51	
Curcas, purging nut			65-66	
Garden cress		Rape oil group	92-95	
Ravison			65-76	
Rape (colza)			55-64	
Black mustard			43	
White mustard			44-49	
Radish seed			51	
Jamba			52	
Small fennel	Non-drying oils		89	
Quince			73	
Cherry kernel			45	
Cherry laurel			44·5	
Apricot kernel			42-46	
Plum kernel			44·7	
Peach kernel			42·5	
Almond			52·5	
Sanguinella			52	
Acorn			60	
Californian nutmeg			77	
Arachis			45-51	
Rice			66·7	
Pistachio			44·7-55	

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[1] K. Wilisch, *Inaug. Diss.*, Augsburg, 1912. The oil was mixed with 70 per cent of paraffin oil (see footnote, p 483) and treated with a 92·5 per cent sulphuric acid.

[2] C. Oettinger and F. Buchta, *Zeit. f. angew. Chem.*, 1911, 828.

Oil.	Class.	Group.	Maumené Test. °C.	
Hazel nut	Non-drying oils		36	
Elozy			69	
Staff tree . . .			77	
Olive			41·5-45	
Coffee berry . . .			54	
Sterculia . . .			158	
Canari			59	
Castor		Castor oil group	46-47	
Menhaden . . .	Marine animal oils	Fish oils	126	
Cod liver . . .		Liver oils	113-116	
Seal		Blubber oils	92	
Whale			92	
Porpoise, body oil . .			50	
Sheep's foot . . .	Terrestrial animal oils		49·5	
Horses' foot . . .			58	
Neat's foot . . .			47-58	

Oil or Fat.	Class.	Group.	Maumené Test. °C.	
Laurel	Vegetable fats		115·6	
Njave			55	
Nutmeg butter . .		Myristica group	39	
Horse fat . . .	Animal fats	Semi-drying	46-54	
Lard		Non-drying	24-41	
Waxes.				Specific Temp. Reaction.
Sperm oil . . .	Liquid waxes		51	100
Arctic sperm oil . .			41-47	93

Undoubtedly, there exists a correlation between the rise of temperature in *Maumené's* test and the iodine value of an oil; the higher the rise of temperature, the higher is the iodine number (cp. Vol. II. Chap. XIV. under "Olive Oil"). However, this correlation cannot be expressed by a constant factor, such as $\frac{\text{Iodine Test}}{\text{Maumené test}}$, for *Hehner and Mitchell*[1] derived from 9 observations (made by one and the same observer) on lards, the factor 1·748; from 10 observations on olive oils, 2·1837; and from 203 observations on olive oils, 2·314. Even on applying the last factor to other oils examined by the same observers, discordant results were obtained.

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[1] *Analyst*, 1895, 147.

An exception to the general rule that the iodine value rises in direct proportion with the *Maumené* test is afforded by sterculia oil (Vol. II. Chap. XIV.), which has an iodine value of 76·6, whereas 158° C. is recorded as its *Maumené test.* This exceptional behaviour would seem to be explained by the fact that sterculia oil forms a solid substance on heating (although castor oil, which simulates sterculia oil in its low iodine value and the property of forming a polymerised oil, does not show a higher rise in temperature than 67° C.).

Oils exhibiting a very marked rise of temperature should be diluted with a measured quantity of olive oil (*Maumené*[1]). *Bishop*[2] recommends mineral oil for the same purpose, and calculates, from the observed rise of temperature, the rise of temperature which the original oil would show in the following manner (which, however, is not quite correct):—Let 67° C. be the rise of temperature obtained with 10 grms. of cod liver oil, 10 grms. of mineral oil, and 20 grms. of sulphuric acid; if the rise of temperature of the mineral oil alone be 14° C., then the figure for cod liver oil would be 2(67 − 14) = 106° C. (*Bishop*).

Bishop obtained in this manner the following results:—

Kind of Oil.	Rise of Temperature calculated. °C.
Cod liver, white	100
„ „ pale	102
„ „ brown	102·5
Arachis	66
Mixture consisting of 80 parts of cod liver oil, pale, and of 20 parts of arachis oil	97
Mineral oil	14

Ellis[3] also recommended mineral oil as a diluent. Having found that no concordant results were obtained when the maximum temperature was much over 60° C. (since above that temperature further reactions set in between sulphuric acid and the oil, cp. Chap. II.), *Ellis* considers it necessary to dilute each oil, if required, with mineral oil in such proportions that the highest temperature attained is below 60° C. For his mode of calculation and his results the original paper must be consulted.

Tortelli, however, has shown that errors are introduced by using mineral oils as diluents, and insists strongly on the exclusive use of olive oil.[4] He further points out that the amount of olive oil added as a diluent must be so adjusted that the final temperature should not exceed 90° C. The apparatus which *Tortelli* uses is described below.

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[1] Cp. also Suzzi, *Boll. Chim. Farm.*, 1905 (44), 301.

[2] *Journ. Pharm. Chem.* 20, 302.

[3] *Journ. Soc. Chem. Ind.*, 1886, 150, 361.

[4] *Chem. Zeit.*, 1909, 126. Cp. also W. H. Boynton and H. C. Sherman, *School of Mines Quarterly*, 1910, 64.

The following example may illustrate the manner in which the thermal number is calculated. Let 43·7° C. be the rise of temperature obtained with an olive oil, and let 63·4° be the rise of temperature observed on examining a mixture consisting of one volume of cameline oil and two volumes of the above olive oil[1]; then the thermal value of the cameline oil is $\left(63{\cdot}4 - \frac{43{\cdot}7 \times 2}{3}\right) \times 3 = 102{\cdot}9°$ C.

Jean[2] determines the heat evolved in *Maumené's* test in a special apparatus, styled by him "Thermelœometer." This apparatus (Fig. 40) consists of a small vessel, A, 4 cm. wide and 6 cm. high, graduated for the reception of 15 c.c. of oil, and of the acid holder B. The latter is fitted with a hollow glass-stopper C, to which is attached the india-rubber tube R. The neck of the acid holder is fastened to a clamp, to which a thermometer is fixed.[3]

The mode of operating is as follows: 15 c.c. of oil, previously warmed to about 40° to 50° C., are placed in A, and 5 c.c. of concentrated sulphuric acid of specific gravity 1·819 are introduced into B. Vessel B is then placed in A, and the apparatus allowed to cool to 30° C., the thermometer being used to stir the oil occasionally. To prevent further cooling, A is placed in the felt-lined brass case E. The acid is then forced out of B through the small syphon-tube into A by blowing through R, and the mixture of oil and acid well stirred until the maximum temperature is reached. Drying oils should previously be mixed with 5 c.c. of mineral oil.

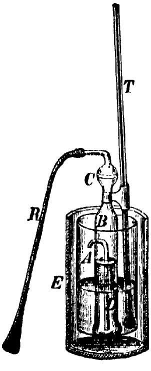

Fig. 40.

Oils containing notable proportions of free fatty acids must be treated with alcohol before testing; a still better plan is to prepare the fatty acids and test the latter. *Jean* obtained the following results with his "thermelæometer":—

Kind of Oil.	Rise of Temperature of the	
	Neutral Oil. °C.	Fatty Acids. °C.
Linseed	61	109
Colza, French . . .	37	44
Colza, Indian . . .	37	46
Olive	41·5	45

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[1] K. Wilisch states, however, that it is best to mix oils giving a strong heat reaction with 70 per cent of paraffin oil, using a 92·5 per cent sulphuric acid. Thus he obtained a maximum rise of temperature. The paraffin oil was the German official "paraffinum liquidum" (of 0·880 specific gravity) which gave no rise of temperature with concentrated sulphuric acid.

[2] *Journ. Soc. Chem. Ind.*, 1890, 1139.

[3] Another apparatus, offering no special feature, was described by Wiley (cp. Wiley, *Lard and Lard Adulterations*, Washington, 1889).

The numbers obtained by *Jean* are not, of course, directly comparable with those given in the foregoing table.

Tortelli[1] proposes another apparatus for determining the *Maumené* number. This apparatus—"thermoleometer"—consists of a glass vessel surrounded with a *Dewar* vacuum-jacketed tube (see p. 490). The thermometer carries near its bulb two pairs of screw paddles (cp. also Fig. 40), which assist in producing the thorough intermixture of acid and oil. The sulphuric acid used has the specific gravity 1·8413 at 15° C. *Tortelli* is of the opinion that the indication furnished by his thermoleometer renders unnecessary the determination of the iodine value of olive oils, it merely being required to multiply the rise of temperature, in degrees centigrade, by 1·83.

The factor 1·83 must, however, not be used for other oils. For non-drying oils having iodine values from 80 to 90, *Tortelli* finds the factor 1·82; for semi-drying oils, of the iodine values from 100 to 110, the factor 1·6 (the actual factor fluctuating between 1·65 and 1·55); for drying oils, of iodine values 125 to 185, the factor 1·48 (the actual numbers varying between 1·55 and 1·40). *Tortelli* is of the opinion that the iodine values as calculated from the thermal values with the aid of these factors are sufficiently accurate for practical purposes. The author, on the contrary, is strongly of the opinion that it would be a mistake to substitute the thermal test for the direct determination of the iodine value.[2] For on the one hand the actual deviations from the several factors as given by *Tortelli* are too numerous and also too great (thus in the case of castor oil the factor is 1·15, and in the case of cotton seed oil 1·40); and on the other hand the analyst must find himself at a loss as to which factor should be applied, if an unknown oil be under examination. In the latter event he would after all be forced to determine first the iodine value.

In the case of solid fats it is inconvenient to bring the sulphuric acid and the fats to the same temperature before commencing the test. *Tortelli* obviates this inconvenience by calculating from the specific heats of the fat and of the acid that temperature at which the two reacting substances have the same temperature. The formula which *Tortelli* gives is based upon the specific heat of olive oil as ascertained by *Regnault*, viz. 0·445. For the values obtained by *Tortelli* in the case of a large number of fats, the reader must be referred to the original paper. It need only be pointed out that the factors for converting them into iodine values vary in the case of solid fats in a much more capricious manner than they do in the case of oils. Thus in the case of vegetable fats the factors vary from 1·67 (for palm oil) to 0·67 (for palm-kernel oil) and even to 0·33 (for cocoa nut oil); and in the case of animal fats from 1·53 (for lard) to 1·04 (for butter fat).

Marcille[3] recommends to weigh the oil, instead of measuring it, and proposes 18 grms. as a suitable quantity.

Exposure to light and air with its concomitant oxidation increases the temperature reaction. Thus *Archbutt* records for a sample of olive oil, which, kept in the dark, gave a *Maumené* test of 41·5° C., the higher figure 52·5° C. after exposure.

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[1] *Boll. Chim. Farm.* Fasc. 6, March 1904; *Chem. Zeit.*, 1909, 125, 134; *Gazz. Chim.*, 1909 (ii.), 71.

[2] Cp. Lewkowitsch, *Jahrbuch der Chem.*, 1904 (xiv.), 438.

[3] *Annal. des Falsific.*, 1909 (2), 230.

This fact is brought out more prominently by *Ballantyne's* observations :—

Kind of Oil.	Rise of Temperature.	
	Original Oil. °C.	After Exposure. °C.
Olive	44	67
Castor	73	78·5
Rape	61·5	72·5
Cotton seed	75·5	100
Arachis	73·5	90
Linseed	113·5	131

It should be noted that the reverse holds good for the iodine absorption numbers.

Thomson and Ballantyne[1] proposed to refer the rise of temperature obtained with 50 grms. of oil and 10 c.c. of sulphuric acid to the rise of temperature which 50 grms. of water give under exactly the same conditions in the same vessel. The quotient $\frac{\text{Rise of temperature with oil}}{\text{Rise of temperature with water}}$ is termed by them "specific temperature reaction"; it expresses, therefore, the rise of temperature compared with water as unity. In the following table the results are multiplied by 100 in order to dispense with decimals. By recording the results in this manner the discrepancies obtained on testing with sulphuric acids of varying strengths are, of course, considerably reduced, as will be seen from the following table :—

Kind of Oil.	Sulphuric Acid of 95·4 per cent.		Sulphuric Acid of 96·8 per cent.		Sulphuric Acid of 99 per cent.	
	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.	Rise in Temperature. °C.	Specific Temperature Reaction.
Olive . .	36·5	95	39·4	95	44·8	96
Olive . .	...	...	39	94	43·8	94
Rape . .	49	127	...	...	58	124
Castor . .	34	88	37	89	...	...
Linseed . .	104·5	270	...	...	125·2	269
Water . .	38·6	100	41·4	100	46·5	100

The following specific temperature reactions are given by *Thomson* and his collaborators, and by *Jenkins* :[2]—

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[1] *Journ. Soc. Chem. Ind.*, 1891, 234.

[2] *Ibid.*, 1897, 194.

Kind of Oil.	Specific Temperature Reaction. Water = 100.		Class of Oil.
	Thomson and Ballantyne.	Jenkins.	
Linseed, Baltic	349		Drying oils
,, East India	320		
,, River Plate	320		
,, raw	...	313	
Japanese wood	...	330	
Menhaden	306	...	Fish oils
Cod liver, medicinal	272	...	Liver oils
,, Scotch	246		
,, Newfoundland	243		
Ling Liver	232[1]		
Coal fish liver	257[1]		
Whiting ,,	317[1]		
Haddock ,,	300[1]		
Skate ,,	322[1]		
Seal	...	278	Blubber oils
,, tinged	229		
,, cold drawn, pale	225		
,, Norwegian	223		
,, steamed, pale	212		
Whale, pale	157		
Cotton seed, refined Egyptian	170	...	Semi-drying oils
,, ,, ,,	169		
,, crude Egyptian	163		
Ravison rape	...	162	
Rape	144		
,,	135		
,,	133		
,,	...	130	
,,	127		
,,	125		
Castor, commercial	89	105	
Sperm, southern	100	...	Liquid waxes
Arctic sperm (Bottlenose)	93	103	
Arachis, commercial	137	...	Non-drying oils
,, French, refined	105		
Olive, Malaga	94		
,, Mogador	93		
,, Mytilene	93		
,, Syrian	93		
,, Candia	92		
,, Gioja	89		
,, commercial	92	94	
Neat's foot	...	87	Animal oils
Linseed, boiled	...	248	Manufactured oils
Blown cotton seed	...	164	
Blown rape	...	153	

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[1] Thomson and Dunlop.

The above-given values have been placed by the author in the order of their magnitude; as was to be expected, the different classes of oils arrange themselves in the same order as in the table given above. It should be pointed out that *Tortelli* [1] reject's *Thomson's* method.

The *Maumené* test and its modifications have been described here in full detail, as this process has been largely used in this country, in France, and in the United States. It still seems to have a certain fascination for some workers, for even up to the present time experiments are being carried out in this direction. Thus *Mitchell* [2] has tried to instil new life into this test by an extended experimental inquiry into the behaviour of glycerides and their fatty acids with concentrated sulphuric acid, carbon tetrachloride being used as a diluent. Furthermore, *Sherman, Danziger, and Kohnstamm*,[3] as also *E. Richter*,[4] and especially *Tortelli* [5] *and Wilisch*,[6] published extensive tables, paying especial attention to the influence of diluents and to the effect of strength of acid. But since, in the author's opinion, the information derived from this test is incommensurate with the labour involved, and since much more definite information can be obtained by the application of the "quantitative reactions," it is considered unnecessary to tabulate the results.

In the majority of cases the analyst can very well dispense with this test altogether. Since *Wijs'* modification of the *Hübl* test permits to ascertain the iodine value in a very short time, the *Maumené* test has lost almost entirely its importance. It will, therefore, only be used in rare cases, when the "quantitative reactions" fail to give a satisfactory and unambiguous answer.

Thus adulterations practised on olive oil can be detected with comparative ease, as olive oil exhibits the lowest rise in temperature excepting the animal oils. It may also offer some slight advantage in the examination of linseed oil for its drying power (cp. also Vol. II. Chap. XIV. "Lard"), and perhaps also in the testing of liquid unsaponifiable matter with a view to differentiating mineral, rosin, and tar oils. But in all these cases it is absolutely necessary to follow *Archbutt's* plan, *i.e.* every observer must construct a table for himself, using oils and fats of known purity, and whenever a sample is tested compare the results with those furnished by the standard sample.

Attempts to derive the composition of a mixture of oils from the *Maumené* test lead to entirely erroneous results.[7]

More reliable results, which can moreover be obtained in a much shorter space of time than by *Maumené's* method and its modifications, are furnished by the *Heat of Bromination Test* (cp. p. 490).

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[1] *Chem. Zeit.*, 1905, 532; 1909, 135.

[2] *Analyst*, 1901, 169.

[3] *Journ. Amer. Chem. Soc.*, 1902, 266.

[4] *Zeits. f. angew. Chem.*, 1907, 1613.

[5] *Chem. Zeit.*, 1909, 134, 171, 184.

[6] *Inaug. Diss.*, Augsburg, 1912.

[7] Cp. W. H. Boynton and H. C. Sherman, *School of Mines Quarterly*, 1910, 64. J. J. Kessler and J. K. Mathiason, *Journ. Ind. Eng. Chem.*, 1911 (3), 66.

(b) *Thermal Reaction with Sulphur Chloride*

Fawsitt[1] proposed to measure the heat evolved by the action of sulphur chloride on various oils, with a view to discriminating between drying and non-drying oils, after the manner of *Maumené's* test. Since, however, this procedure offers no advantage over *Maumené's* test, or the *Heat of Bromination Test* (p. 490), it must suffice to briefly describe the *modus operandi*, and to record the values obtained in the table given below.

Thirty grams of the sample are weighed in a small beaker; this is then placed in a larger one, the space between the two beakers being packed with cotton wool. A thermometer is inserted into the oil, the temperature is read off, and the sulphur chloride poured in slowly, with constant stirring. The time is then taken, and the thermometer kept stationary until the mercury ceases to rise. The highest temperature and the time are noted.

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[1] *Journ. Soc. Chem. Ind.*, 1888, 552.

Class of Oil.	Kind of Oil.	Number of c.c. S_2Cl_2 added.	Rise in Temperature.	Time in Rising.	Rise per Minute.	Final Condition of Oil.
			°C.	Min.	°C.	
Drying oils .	Linseed	2	57	5	11·4	Liquid, viscous
	,,	3	79	3	26·3	,, very viscous
	,,	4	97	2	48·7	Solid, sticky
Liver oils .	Cod liver	2	55	4	13·7	Liquid, viscous
	,, ,,	3	82	3	27·3	Solid, very sticky
	,, ,,	4	103	3	34·3	,, dry
Blubber oils .	Seal	2	45	10	4·4	Liquid, more viscous
	,,	3	79	6	13·2	Solid, sticky
	,,	4	112	5	22·4	,, dry
	Whale	2	57	6	9·4	Liquid, more viscous
	,,	3	71	5	14·1	,, very viscous
	,,	4	91	3	30·2	Solid, dry
Semi-drying oils	Cotton seed	2	49	11	4·4	Liquid, more viscous
	,,	3	64	9	7·1	,, very viscous
	,,	4	93	6	15·4	Solid, sticky
	Rape	2	53	10	5·3	Liquid, more viscous
	,,	3	66	7	9·3	Solid, slightly sticky
	,,	4	89	6	14·8	,, dry
Non-drying oils	Olive	2	52	6	8·7	Liquid, viscous
	,,	3	69	5	13·7	,, very viscous
	,,	4	94	4	23·5	Solid, dry
	Castor	2	56	2	27·7	Liquid, very viscous
Liquid waxes .	Sperm	2	37	16	2·3	Liquid
	,,	3	54	11	4·9	Liquid, more viscous
	,,	4	71	8	8·8	,, ,, ,,
	,,	5	86	6	14·2	,, very viscous
Animal oils .	Neat's foot	2	51	7	7·3	Liquid, more viscous
	,,	3	66	5	13·2	,, very viscous
	,,	4	82	4	20·5	Solid, sticky
	Lard	2	40	16	2·4	Liquid, very viscous
	,,	3	62	9	6·9	Solid, became dry on standing
	Oleic acid	2	53	6	10·6	Liquid, viscous
	,, ,,	3	74	5	14·9	,, ,,
	,, ,,	4	99	6	16·5	,, ,,
	Stearic acid	2	5 [1]	7	0·7	Solid
	,, ,,	4	8 [1]	5	1·6	,,
	Glycerol	4	21	7	3·0	Liquid

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[1] Initial temperature, 65° C.

(c) *Thermal Reaction with Bromine; Heat of Bromination Test. Bromine Thermal Value*

The action of bromine on oils and fats is attended with considerable evolution of heat. *Hehner and Mitchell*[1] showed that the measurement of the heat thus evolved leads to results furnishing more definite data than are obtained in the *Maumené* test. The following are the details of the method :—

One gram of oil is placed in a *Dewar* vacuum-jacketed test-tube[2] and dissolved in 10 c.c. of chloroform (in order to moderate the action). Exactly 1 c.c. of bromine, measured by means of a pipette (provided at its upper end with a narrow tube filled with caustic lime, and having an asbestos plug at each end), and previously brought to the same temperature as the oil in the vacuum tube, is run in. The instantaneous rise of temperature is measured by means of a correct thermometer divided into fifths of a degree centigrade.

The whole operation occupies only a few minutes. (Fatty acids are best dissolved in glacial acetic acid, and treated as above.)

Hehner and Mitchell compared the numbers obtained for the rise of temperature of various oils and fats with the iodine numbers, in order to elucidate the correlation (if any) existing between these two values. As will be seen from the following table, the factor 5·5 serves to express the relation with considerable accuracy for the majority of the fatty substances examined by them under the particular conditions. The column headed "Deviation" has been added by the author.

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[1] *Analyst*, 1895, 148.

[2] The oil may be weighed in the tube, suspended by means of a platinum wire from the arm of the balance (cp. Archbutt, *Journ. Soc. Chem. Ind.*, 1897, 310). In their earlier experiments Hehner and Mitchell employed an ordinary test-tube packed into a beaker with cotton wool; the results thus obtained are, *cæteris paribus*, two degrees centigrade lower.

[TABLE

I. Oil or Fat.	II. Heat of Bromination.	III. Iodine Number.		IV. Deviation.	
	°C.	Experiment.	Calculated from Column II. by multiplying by 5·5.	Absol.	Per cent.
Lard, No. 1	10·6	57·15	58·3	+1·15	+2·00
,, 2	10·4	57·13	57·2	+0·07	+0·12
,, 3	11·2	63·11	61·6	−1·51	−2·40
,, 4	11·2	61·49	61·6	+0·11	+0·18
,, 5	11·8	64·69	64·9	+0·21	+0·32
,, 6	11·8	63·96	64·9	+0·94	+1·50
,, 7	10·2	57·15	56·1	−1·05	−1·90
,, 8	10·4	57·80	57·2	−0·60	−1·05
,, 9	9·0	50·38	49·5	−0·88	−1·70
,, 10	11·0	58·84	60·5	+1·66	+2·7
,, +10 per cent cotton seed oil .	11·6	64·13	63·8	−0·33	−0·52
Lard fatty acids	10·4	59·60	57·2	−2·40	−4·20
,, ,, ...	11·0	59·15	60·5	+0·35	+0·57
Mutton fat (kidney) . . .	8·1	44·48	44·5	+0·02	+0·05
,, ,, (flare)	7·6	39·70	41·8	+2·10	+5·0
Butter, No. 1	6·6	37·07	36·3	−0·77	−2·1
,, No. 2	7·0	38·60	38·5	−0·10	−0·27
,, fatty acids . . .	6·2	36·50	34·1	−2·40	−7·04
Almond oil	17·6	96·64	96·68	+0·04	+0·041
Olive oil	15·0	80·76	82·50	+1·74	+2·1
Maize oil	21·5	122·0	118·20	−3·80	−3·2
Cotton seed oil	19·4	107·13	106·70	−0·43	−0·4
Castor oil	15·0	83·77	82·50	−1·27	−1·5
Linseed oil, No. 1	30·4	160·7	167·20	+6·5	+3·9
,, ,, No. 2	31·3	154·9	172·00	+17·1	+10·0
Rape oil, No. 1	18·4	88·33	101·20	+12·87	+12·7
,, ,, No. 2	17·6	77·2	96·80	+19·6	+20·0
Cod liver oil	28·0	144·03	140·00	−4·03	−2·9
,, ,, ...	19·0	108·5	104·5	−4·00	−3·8
,, ,, (commercial) . .	19·2	105·7	105·6	−0·01	−0·009
,, ,, ,, . .	18·9	105·7	103·9	−1·8	−1·7

It should be distinctly understood that the factor 5·5 must not be taken as an absolute one, but as depending on the particular vacuum-tube and the *modus operandi* adopted by *Hehner and Mitchell.* It is therefore imperative that each chemist who uses this method should ascertain the factor applying to his individual case by determining the heat of bromination of a non-drying oil, the iodine value of which has been ascertained by *Hübl's* (or *Wijs'*) method.

Thus *Jenkins*[1] obtained the factor 5·7; *Archbutt*[2] found it to vary in the case of tallow, olive oil, rape oil, and linseed oil from 5·7 to 6·2. In the latter case the variation may be partly due to the fact that the weight of substance taken was not the same in every instance.

Notwithstanding the considerable differences which linseed and rape oils show, *Hehner and Mitchell* thought that the determination of the iodine number by *Hübl's* method might be replaced by that of the heat of bromination. They even went so far as to express the opinion that the *calculated* iodine values of the examined linseed and rape oils are more correct than those found by *Hübl's* method. In the author's opinion this is tantamount to begging the question, for a much larger number of experiments is required to substantiate such far-reaching conclusions. This is all the more necessary as serious deviations have been stated by *Jenkins* for tung oil and for " blown oils."

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[1] *Journ. Soc. Chem. Ind.*, 1897, 194.

[2] *Ibid.*, 1897, 310. Cp. also Wilson, *Chem. News*, 1896, 27.

On account of the exceeding simplicity of this test, and the rapidity of its execution, the heat of bromination test may prove a useful auxiliary test, especially where a large number of specimens of the same kind have to be examined in a short time. It will be no less useful as a sorting test (*Hehner*), in so far as it affords rapid information as to the class to which an oil belongs. Its great rapidity being one of the chief recommendations in favour of using the test, *Wiley's*[1] modification (a chloroformic solution of bromine) would seem to complicate matters, all the more so as a lowering of temperature takes place when bromine is dissolved in chloroform. The latter fact has already led to the suggestion to substitute carbon tetrachloride for chloroform. In the case of oils giving a violent reaction (linseed oil), *Archbutt*[2] suggests to work with 0·5 grm. of oil, and to multiply the result by 2, and in the case of solid fats, which develop but little heat, to take 2 grms., and divide the result by 2.

Recently *A. Heiduschka and E. Rheinberger*[3] published a study on the bromine-thermal test, wherein they describe a special apparatus. They also worked with different solvents and confirmed that chloroform is the most suitable solvent.

Since the introduction of *Wijs'* modification of the *Hübl* test, hardly more time is required for the determination of the iodine value than the *Heat of Bromination test* demands. Hence the latter has fallen into desuetude, and may be entirely dispensed with, even in a works laboratory.

The heat of bromination test has been applied by *Klamroth* to the examination of mixtures of cholesterol-, sitosterol-, and stigmasterol-acetates (cp. Chap. IX. p. 597).

6. Colour Tests

A very large number of colour reactions have been proposed from time to time, and are still being proposed, for the recognition of individual oils.

A complete synopsis of the older methods has been given by *Chateau* in his work *On Fats.*[4] The following tests, some of which are, curiously enough, still being employed by some writers, may be mentioned in chronological order :—

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[1] *Journ. Soc. Chem. Ind.*, 1896, 384.

[2] *Ibid.*, 1897, 310.

[3] *Pharm. Zentralhalle*, 1912, 303.

[4] Th. Chateau, *Traité complet des Corps Gras Industriels*, Paris, 1863 (Bance et Mallet-Bachelier). Translated into German under the title, *Fette ; bearbeitet von H. Hartmann.* Leipzig, 1864.

Fauré (1839) stated that vegetable oils can be distinguished from animal oils by gaseous chlorine; the latter oils—with the exception of foot oils from terrestrial animals—are said to become black on treatment with this reagent. *Fauré* also employed ammonia as a general reagent.

Heydenreich (1848) first applied concentrated sulphuric acid to the examination of oils; his method consisted in allowing five drops of the oil under examination to fall on the surface of pure, concentrated sulphuric acid in a porcelain basin, and observing the colours developed in the first three minutes.

Penot introduced sulphuric acid saturated with potassium bichromate as a general reagent; the colours obtained with different oils were considered by him to be characteristic of these oils.

Behrens used a mixture of equal parts of sulphuric and nitric acids.

Crace Calvert's (1854) method has for a long time been in vogue. He described the colour reactions observed on treating different oils with the following reagents: (1) caustic soda, 1·340 spec. grav.; (2) sulphuric acid, 1·475 spec. grav.; (3) sulphuric acid, 1·530 spec. grav.; (4) sulphuric acid, 1·635 spec. grav.; (5) nitric acid, 1·180 spec. grav.; (6) nitric acid, 1·220 spec. grav.; (7) nitric acid, 1·330 spec. grav., and subsequently caustic soda, 1·340 spec. grav.; (8) syrupy phosphoric acid; (9) a mixture of equal volumes of nitric acid, spec. grav. 1·330, and sulphuric acid, spec. grav. 1·345; (10) aqua regia, consisting of 25 measures of hydrochloric acid and 1 measure of nitric acid, spec. grav. 1·330, and subsequent treatment with caustic soda. In some text-books *Crace Calvert's* results are presented in a tabular form; for reasons stated below the table is omitted in this work.

Hauchecour-Yvetot proposed hydrogen peroxide as a general reagent.

Chateau, in his book *On Fats*, published very extensive tables, purporting to distinguish the oils by systematic application of the following reagents: (*a*) calcium polysulphide, (*b*) zinc chloride, (*c*) concentrated sulphuric acid, (*d*) fuming stannic-chloride, (*e*) syrupy phosphoric acid, (*f*) phosphoric acid, (*g*) mercuric nitrate, with subsequent addition of sulphuric acid, (*h*) mercuric nitrate alone. All these tests must, on the whole, be considered as having no value; hence they are not recorded here.

Glaessner (1873) also proposed a systematic examination of oils, using as reagents caustic potash, fuming nitric acid, and concentrated sulphuric acid.

In order to avoid the rise of temperature caused by the concentrated sulphuric acid (see "*Maumené* test," p. 478), whereby some characteristic colour reactions become indistinct, or the oil becomes partially charred, *Finkener* dilutes the oils with carbon bisulphide, when no thermal reaction is stated to take place.

All colour reactions must be used with the greatest circumspection, as small amounts of cholesterol, sitosterol, and, further, minute quantities of resinous or albuminoid substances, or other foreign matters, influence the colourations to such an extent that in most cases it must remain doubtful whether the reactions are really characteristic of the oils themselves. A notable example of how colour reactions may become misleading is best exemplified by the fact that a serious mistake was made in declaring an imperfectly purified tallow as adulterated, because it gave with nitric acid a reddish-brown colouration which was judged to be due to the presence of cotton seed stearine.

Colour reactions were formerly resorted to for lack of better methods, but have been superseded in the majority of cases by the "quantitative reactions." It should be borne in mind that many colour reactions quoted in older text-books, and perpetuated in even more modern treatises, were not always obtained with typical samples, little or no regard having been paid to their source, their mode of purification, their age, and all that host of circumstances which have a vital influence on the colour produced by the reagents. In consequence of progress made in the technical preparation of oils and fats, a large number of impurities, which were actually the very substances that gave origin to the colours supposed to be characteristic of the oils or fats, have ceased to occur in commercial samples.

A colour reaction can only then be considered of some value if it be produced by a well-defined substance, occurring naturally in an oil or fat, and characteristic of it to such an extent that the sample may be identified by that reaction. Obviously, these characteristic substances which only occur in minute quantities should not be easily removable in the course of the usual manufacturing processes.

As a type of a most valuable reaction of this kind I refer to *Baudouin's* test, originally proposed by *Camoin*, for sesamé oil, which has found its scientific explanation and confirmation in the isolation of the chromogenetic substance in that oil (cp. Vol. II. Chap. XIV. "Sesamé Oil"). But even in this case great care is required to guard against errors[1] that may be caused by similar colour reactions such as are given by certain Tunisian olive oils (cp. Vol. II. Chap. XIV. "Olive Oil"), and by certain colouring matters which are added to margarines (cp. Vol. II. Chap. XIV. "Sesamé Oil," "Butter Fat"). The colour reaction of cholesterol and its congeners, although highly characteristic, requires much more circumspection in its interpretation, as other substances also give the same or a very similar colouration.

Group reagents, such as are used in inorganic analysis, do not exist in fat analysis, and every new reagent recommended as such must be received with great suspicion.

The author[2] fully examined four of the so-called group reagents, viz. concentrated sulphuric acid, gaseous chlorine, syrupy phosphoric acid, and phospho-molybdic acid. The following conclusions were drawn:—

Sulphuric Acid.—This reagent enables, at best, with a good deal of practice, to discriminate between drying, semi-drying, and non-drying oils, if the acid be applied to the oil direct. Drying oils may be recognised by their forming dark clots when two drops of concentrated acid are stirred into twenty drops of oil. A discrimination between semi-drying and non-drying oils, however, is more difficult, and indeed scarcely possible in every case.

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[1] Cp. also colour reactions of some ethereal oils, R. Reich, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xvi. 453.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1894, 617.

The better an oil dries, the darker is the colour produced by the acid. Judging from the depth of the colour it may be possible to distinguish between oils standing at the extreme ends of these classes, such as cotton seed oil and olive oil, whereas, to take an example, it is impossible to differentiate, by this test alone, rape oil from cotton seed oil. The colour reactions obtained with a solution of an oil in carbon bisulphide cannot be said to yield more reliable results, the dilution tending to obliterate the otherwise sharp distinction between the eminently drying oils and the other oils.

In the case of liver oils, the blue and purple colourations due to the presence of cholesterol and colouring principles—lipochromes—are very characteristic; they are best observed if the oil be previously dissolved in carbon bisulphide. The value of this test is, however, greatly diminished by the fact that some blubber oils show a similar reaction. The author formerly ascribed this to an accidental admixture with liver oils, which is very likely to occur on board whaling vessels, where all kinds of fatty material obtained during a voyage are mixed together. *Thomson and Dunlop*, however, observed in the case of one specimen of seal oil and of one specimen of porpoise oil, both of undoubted genuineness, the characteristic colour reaction of liver oils (see Vol. II. Chap. XIV. "Liver Oils"); yet the author was unable to obtain such an exceptional colour reaction with a very large number of seal oils the purity of which there was no reason to doubt. It should also be borne in mind that with the setting in of rancidity the chromogenetic substances are frequently destroyed.

Chlorine gas is by no means a group reagent for marine animal oils. The black colour which is obtained with chlorine depends entirely on the state of purity and rancidity of the oils. Hence even vegetable oils or terrestrial animal oils may furnish stronger colourations than pure liver oils.

Phosphoric acid indicates only impurities that can be eliminated by refining, or products of oxidation formed after rancidity has set in.

Phospho-molybdic Acid.—This reagent was proposed by *Welmans*,[1] and has met with more attention than the results obtained with it deserve. The test is performed as follows:—1 grm. (or 25 drops) of an oil or fat is dissolved in 5 c.c. of chloroform in a test-tube, and agitated with 2 c.c. of a freshly-prepared solution of phospho-molybdic acid,[2] or of sodium phospho-molybdate and a few drops of nitric acid. After standing for a short time the chloroformic layer becomes colourless, whereas the upper layer shows, in the case of a vegetable oil and of cod liver oil, according to *Welmans*, a green colour. On adding ammonia or a fixed alkali a beautiful blue colour appears, the intensity of which corresponds to that of the green tint noticed before. Animal fats—with the above-mentioned exception of cod liver oil—were stated to cause no reduction, and consequently to produce no green with subsequent blue colouration.

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[1] *Journ. Soc. Chem. Ind.*, 1892, 548.

[2] The reagent is prepared by precipitating a solution of ammonium molybdate with sodium phosphate, washing the precipitate thoroughly and dissolving it in a warm solution of sodium carbonate. The solution is boiled down to dryness and the residue heated. If the residue becomes coloured blue, add a few drops of nitric acid and heat again. Then boil the residue with water, add nitric acid until strongly acid, and dilute so as to obtain a ten per cent solution. Filter if necessary, and keep the reagent pro-

The green colour is due, according to *Welmans*,[1] to a mixture of the yellow reagent with the blue reduction product. If the yellow colour be taken away by adding ammonia, blue remains.

The author's experiments,[2] however, demonstrated that such a distinction cannot be upheld. Several kinds of olive oil, as also almond, arachis, and peach oils, showed far less distinct colours than tallow oil, and even lard oil. Amongst the large number of oils and fats of undoubted genuineness, and belonging to all classes of oils and fats, examined by the author, only pure, freshly rendered lard left the phospho-molybdic acid unreduced, so that it remained colourless on being supersaturated with ammonia. But a slightly rancid lard behaved almost like a vegetable oil in *Welmans*' test. As *Welmans*' reaction was prescribed officially in Germany (up to 1908) as a test for the rapid detection of vegetable oils and fats in animal oils and fats, the author wishes to emphasise that this test breaks down completely in the case of vegetable oils which have been refined with sulphuric acid. Vegetable oils are also apt to lose in course of time the property of giving the *Welmans*' reaction. This is, of course, due to the chromogenetic substance in the oils becoming changed under the influence of light. Moreover, mineral oils and rosin oils give deep colourations. The phospho-molybdic acid test can, therefore, at best only rank amongst preliminary tests.

Bellier's reagent is now prescribed officially in Germany, in place of *Welmans*', for the detection of vegetable oils in lard. According to the official directions 5 c.c. of (melted and filtered) lard are shaken vigorously, at a temperature not exceeding 35° C., with 5 c.c. of colourless nitric acid of specific gravity of 1·4 and 5 c.c. of a saturated solution of resorcinol in benzene in a thick-walled glass-stoppered test-tube for 5 seconds. If during the shaking or within 5 seconds after the shaking a red, or violet, or green colour appears, the presence of vegetable oils is assumed. If after the lapse of 5 seconds the colour appears, it is disregarded. It is obvious that any reducing substance present will produce a colour owing to a reducing action taking place and need not necessarily indicate a vegetable oil. Thus *J. Royer*[3] has shown

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tected from dust. A modification of the Welmans' reagent is Serger's reagent (0·1 grm. of sodium molybdate dissolved in 10 c.c. of concentrated sulphuric acid); cp. Utz, *Chem. Revue*, 1912, 128.

[1] *Zeits. f. öffentl. Chem.* 6, 127.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1894, 1619.

[3] *Annal. des Falsific.*, 1910, 380; cp. also A. Olig and E. Brust, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 561.

that while cold pressed poppy seed oil does not give a colouration with *Bellier's* reagent, the "second," hot pressed oil gives a distinct colouration.

Unfortunately the tendency to ascribe decisive importance to colour reactions has been on the increase during recent years, and a very large number of papers have been published attempting to attribute an entirely unwarranted meaning to colour reactions.[1] Thus, to give an example, the *Liebermann-Storch* reaction (see p. 610) and a reaction with trichloroacetic acid have been interpreted to point to the occurrence of cholesterol in crude petroleums,[2] in beeswax, etc., without any further facts being adduced to substantiate such far-reaching conclusions. Latterly *Halphen* [3] attempted to base a classification of oils and fats on colour reactions.

In the opinion of the author all these endeavours, if hastily expanded into generalisations, without carefully considering all possible causes that may defeat the colour tests (such as traces of decolourising agents left in the oils and fats), must lead to failure and confusion; hence a full digest of, or even full reference [4] to these papers is omitted here.

Those colour reactions which have been useful in special cases for the identification of an oil or for the detection of an adulterant will be exhaustively dealt with in Volume II. Chapter XIV. when treating of the distinctive properties of the individual natural oils and fats. It may, therefore, suffice here to enumerate them briefly:

(1) *Baudouin's* (*Camoin's*) test for sesamé oil (see Vol. II. "Sesamé Oil").

(2) *Halphen's* colour test for cotton seed oil, kapok oil, and baobab oil (see Vol. II. "Cotton Seed Oil").

(3) *Becchi's* colour test for cotton seed oil; although less reliable than *Halphen's* test, it is still largely used in France and Italy (see Vol. II. "Cotton Seed Oil").

(4) *Nitric Acid* test for cotton seed oil (see Vol. II. Chap. XIV. "Cotton Seed Oil").

(5) *Sulphuric Acid* test for liver oils (see Vol. II. Chap. XIV. "Liver Oils").

(6) *Liebermann-Storch* test for rosin, see Chap. X.

It must, however, be emphasized again that even these colour reactions depend on the presence of foreign substances, and that with their removal or chemical change in their composition the colour reactions cease to be operative. Thus, when cod liver oil and cotton seed oil, to take the two most prominent oils containing characteristic chromogenetic substances, are subjected to the catalytic process of hydrogenation (see Chap. I. p. 59, Vol. III. Chap. XV. "Hydrogenised Fats"), the treated products no longer exhibit the characteristic colour reactions mentioned above.

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[1] Cp. Th. Merl, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 529.

[2] Cp. Vol. III. Chap. XVI.

[3] *Atti del VI. Congres. Internazionale*, 1907, vol. v. p. 630.

[4] Colour tests are even being proposed for the qualitative detection of mineral oil (F. Schulz, *Chem. Zeit.*, 1908, 345; cp. Charitschkoff, *Chem. Revue*, 1908, 315).

Hydrogenised sesamé oil behaves somewhat capriciously in the colour test, some specimens retaining the chromogenetic substance unchanged, whereas others no longer give the *Baudouin* reaction.

CHAPTER VIII

EXAMINATION OF MIXED FATTY ACIDS

If the quantitative and qualitative reactions described in the two preceding chapters have not led to sufficient information, and hence it becomes desirable to gain further insight into the composition of the individual esters—glycerides in the case of oils and fats, or esters of monohydric alcohols in the case of waxes—the necessity arises to examine the *mixed fatty acids*. The problem is somewhat simpler in the case of glycerides than where waxes are concerned, as the basic constituent of all the glycerides—glycerol—can be easily removed after saponification has been carried out. A complication arises if we have to take into account a notable amount of soluble fatty acids, the presence of which is indicated by a high saponification value (exceeding 200) and a high *Reichert-Meissl* value (exceeding 2) of the sample. Such a case will be specially considered under Section B of this chapter.

The mixed *insoluble* fatty acids of fats and waxes are prepared according to the directions given (Chap. III. p. 110). Oils and fats contain small amounts of unsaponifiable matter, as has been explained already (cp. also below, p. 584). If the unsaponifiable matter does not exceed 0·5 per cent or, at most, 1 per cent, it may, as a rule, be neglected; otherwise the unsaponifiable matter must be separated from the soap solution before the fatty acids are isolated.

This is imperative in the case of waxes, the alcoholic constituents of which form about 50 per cent of the total mass.

The separation of the unsaponifiable substances from the fatty acids is effected in the manner described in Chapter VI. under "Unsaponifiable Matter."

In the following sections an attempt is made to describe, in a systematic manner, the methods applicable to the examination of the isolated fatty acids, following, as far as possible, the order adopted in Chapters V. and VI. On the whole, the physical methods of examination afford similar information to that obtained in the case of the fats and waxes themselves; still, in some special cases additional indications are furnished which may be of great assistance in the examination. Most of the chemical methods admit of the quantitative or, at least, approximate estimation of the several constituents.

A. PHYSICAL METHODS

Specific Gravity

The specific gravity of the mixed fatty acids hardly affords more detailed information than is obtained by the examination of the corresponding oils and fats themselves. It is, therefore, considered unnecessary to collate in a table the published specific gravities of the mixed fatty acids. The numbers will be found in the tables of physical and chemical characteristics of the fatty acids of the oils and fats described in Vol. II. Chap. XIV.

Melting and Solidifying Points

The *melting points* of fatty acids are much more characteristic than those of the corresponding oils and fats; nevertheless, they do not afford information of such discriminative value as is obtained by the determination of the solidifying point. Hence it is not considered necessary to collate in a table the melting points of the mixed fatty acids, and the reader is referred to the detailed indications given for each individual product in Vol. II. Chap. XIV. under the headings "Physical and Chemical Characteristics of the Insoluble Fatty Acids."

The determination of the melting point is usually carried out in a capillary tube (Chap. V.). In the case of high melting fatty acids, such as tetrabromides, hexabromides, and octobromides of the fatty acids, it is convenient to insert the capillary tube (fastened to the thermometer in a suitable manner) in a small distilling flask, half filled with concentrated sulphuric acid or glycerin. Any vapours distilling over can be condensed and collected.

Much more characteristic than the melting point is the *solidifying point* of the fatty acids. If observed under strictly comparable conditions, valuable information of a discriminative nature can thus be obtained even on using the mixed fatty acids as they result on saponification, or, if need be, after elimination of the unsaponifiable matter.

Dalican proposed a method for the determination of the solidifying point of the insoluble mixed fatty acids, which has been adopted in this country, in the United States, and in France for the commercial examination and valuation of fats. It is known under the name of "Titer Test," and gives, as the author can testify from his own experience, reliable and, as shown by repeated observations, constant results, provided the test be made carefully, according to the following details. (The number ascertained as the solidifying point is not a physical constant, as it depends on the rate of cooling of a definite quantity examined under certain conditions.) 50 grms. of the fat under examination are saponified (cp. p. 109), the separated fatty acids are freed from water and finally filtered through a dry plaited filter into a small porcelain dish. The fatty acids are allowed to solidify and to stand over night under a desiccator. The fatty substance is carefully melted in an air-bath or over a free flame, and as much of it is poured into a test-tube, 16 cm. long and 3·5 cm. wide, as will fill the tube more than half full. The tube is then fastened by means of a cork into a wide-mouthed bottle, 10 cm. wide and 13 cm. high, and an accurate thermometer (graduated in tenths of degrees from about −5° C. to 60° C., having a mercury bulb about 3 cm. long and 6 mm. in diameter, and carefully standardised with the aid of a "normal thermometer") is inserted in the fatty acids, so that the bulb is in the centre of the mass. When a few crystals appear at the bottom of the tube, the mass is stirred by giving the thermometer a rotary movement, first three times from right to left, and then three times from left to right. Next stir continually, with a quick circular movement of the thermometer, without allowing it to touch the sides of the vessel, and taking care that all solidified portions, as they form, are well stirred into the mass until the latter has become cloudy throughout. The thermometer should now be observed carefully. A good plan is to write down the temperature at short intervals. At first the mercury will continue to fall, or at least remain stationary, then it will rise suddenly some tenths of a degree and reach a maximum, remaining stationary thereat for some little time before it falls again. This point is called the **"titer" or solidifying point** of the mixed fatty acids. In the case of dark coloured fats it may be impossible to observe the separation of crystalline matter. In such cases it is best to make a preliminary experiment which affords the necessary guidance for the final observation.

Finkener[1] does not consider this a satisfactory method, whereas, in the opinion of the author, as stated already, it forms a reliable basis for the commercial valuation of solid fats, provided the fatty acids have been dried in the manner described. *Finkener* uses *larger* quantities in small globular flasks of about 50 mm. diameter; in order to prevent rapid cooling he places the vessel filled with the melted acids in a wooden box[2] (Fig. 41). (The same apparatus is also recommended by him for the determination of the solidifying points of commercial tallows.) The solidifying points found by *Finkener* are higher than those obtained by *Dalican*. *Finkener's* apparatus has been adopted by the German Custom House officials.

Higher solidifying points—by 0·2° to 0·3° C.—are obtained when the fatty acids are previously heated for two hours at 100° C., a procedure proposed by *Wolfbauer*.[3] His method has been adopted in Austria for the determination of the "titer" of tallow and palm oil, and it is therefore described in full, although it suffers somewhat from over-elaboration.

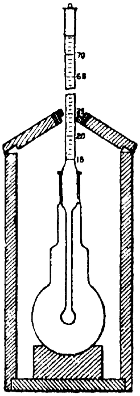

Fig. 41.

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[1] *Journ. Soc. Chem. Ind.*, 1889, 424.

[2] *Ibid.*, 1890, 1071.

[3] *Ibid.*, 1894, 181, 908.

120 grms. of fat are melted in a beaker at a temperature slightly above the melting point, mixed with 45 c.c. of a caustic potash solution (1250 grms. of caustic potash in one litre of water), and stirred until the fat is completely emulsified. It is then covered and kept at 100° C. for two hours, with occasional stirring. A small portion is then tested by warming with 50 per cent alcohol—to ascertain whether saponification is complete; a clear solution should result. The soap is then decomposed by boiling with 165 c.c. of dilute sulphuric acid, specific gravity 1·142, preferably in a silver dish, until the free fatty acids rise to the top as a clear oily layer. The silver dish is covered with a flat dish filled with cold water, to check evaporation. The aqueous solution is completely drawn off, and the fatty acids are washed by boiling for one-quarter of an hour with dilute sulphuric acid (5 c.c. of concentrated sulphuric acid and 100 c.c. of water). After allowing to settle and removing the dilute acid, the fatty acids are boiled with 100 c.c. of distilled water, and washed until the wash-waters are no longer acid. The fatty acids are then dried in an open dish at 100° C. for two hours.

In the determination proper, the following apparatus is employed: a thin-walled test-tube, 3·5 [1] cm. by 15 cm., is fixed in a suitable bottle by means of a cork. A centigrade thermometer, extending from 1° to 60° C., and graduated in fifths of a degree, is fixed in the test-tube by means of a cork, which must be sufficiently loose to permit of easy stirring of the contents of the tube with the thermometer. As the thermometer should be as short as possible, its scale is shortened by an enlargement blown in the bore of the capillary somewhere between 2° and 28° C. The amount of mercury *above* the surface of the fatty acid is thus diminished, and an appreciable error is said to be thereby avoided. The test-tube is then filled to within 1 cm., or 1·5 cm., of the top with the melted fatty acids, the thermometer is immersed in the liquid to about the 35° mark (when the instrument should clear the bottom of the tube by about 4 cm. or 5 cm.), and the liquid is stirred until it becomes quite opaque, and partial solidification sets in. Care should be taken at this point that the thermometer be not more deeply immersed than before, and after stirring rapidly in a circle ten more times, the temperature is observed. The mercury now begins to rise; the highest temperature noted is taken as the solidifying point.

The reading of the thermometer should be corrected for its inherent errors by comparison with a standard instrument. Its zero point should also be redetermined from time to time. Each determination should be repeated, and the difference between the duplicate experiments should not exceed 0·1° C.; as a rule, it will not exceed 0·05° C.[2]

For reasons explained above it might appear doubtful whether *Wolfbauer's* higher values are due to removal of the last traces of adhering moisture, or to such slight changes of the fatty acids as occur whilst drying. This doubt has been removed by the fact that *Shukoff* obtained practically the same numbers by a method in which heating of the fatty acids is avoided (see below).

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[1] In a narrower tube, about 2·5 cm. in diameter, the solidifying point was found to be lower by 0·20° C.

[2] For *Garrigues'* "method" cp. *Journ. Soc. Chem. Ind.*, 1895, 280.

The Association of Official Agricultural Chemists in the United States of America have examined the various modifications of *Dalican's* test, proposed by *Finkener*, *Wolfbauer*, *Boyce*, *Wesson*, and others, and the report on the co-operative work has been published by *L. M. Tolman* in Circular No. 22 of the United States Department of Agriculture, Bureau of Chemistry. The following lines give an abbreviated description of the *modus operandi* recommended :—

Saponify 75 grms. of fat in a metal dish with 60 c.c. of 30 per cent (36° Bé.) sodium hydroxide solution and 75 c.c. of 95 per cent (by vol.) alcohol and 120 c.c. of water. Boil to dryness, with constant stirring to prevent burning or scorching, over a very low flame, or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used, boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 c.c. of 30 per cent sulphuric acid (25° Bé.) to free the fatty acids, and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam-bath until the water has settled and the fatty acids are clear ; then decant them into a dry beaker, filter, using a hot-water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to a test-tube, which is 25 mm. in diameter and 100 mm. in length (1 by 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce "saltmouth" bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2·8 by 6 inches), fitted with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend a thermometer[1] graduated to 0·10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the centre of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

The following conclusions were drawn by the Reporter of the Association :—The method of preparing the fatty acids has no influence on the results. The fatty acids should be dry ; it is recommended to filter the fatty acids and to heat them for twenty minutes at 100° C. The varying results obtained by various chemists are chiefly due to differences in methods of stirring the fatty acids during the test.

[1] The official American directions give the following elaborate description of the thermometer to be used :—"The thermometer must be graduated in tenth degrees from 10° to 20°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about 15 inches over all. The thermometer is annealed for 75 hours at 450° C., and the bulb is of Jena normal 16^{III} glass, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer glass."

Shukoff at first proposed to determine the "titer test" in a tube 3 cm. in diameter, surrounded by a *Dewar* vacuum mantle, the outer diameter of which is 5 cm. and the height 10 cm. The fatty acids are poured into the inner tube, which is then closed by a cork fitted with a delicate thermometer. About 5° C. above the expected "titer," the vessel is agitated in an up-and-downward direction somewhat energetically, until the contents have become distinctly turbid. The observation is then made in the manner described above. Later on *Shukoff*[1] showed that the vacuum mantle can be dispensed with, since equally good results are obtained, if a tube of 2½ to 3 cm. diameter is fitted with a thermometer, and then fixed by means of a cork in a wide-mouthed bottle. The results so found are stated to be in close agreement with the numbers obtained by *Wolfbauer's* procedure.

It is obvious that by varying the conditions under which the "titer test" is taken different results will be obtained. Hence there does not appear to be so much need for working out a new method as for agreeing on a certain *modus operandi*, and adhering to it strictly. *Dalican's* method, with the modifications as described by the author (p. 501), has proved itself reliable in the author's own experience, extending over a great number of years; even different observers in the author's laboratory do not obtain greater variations than about 0·1° C. This is quite satisfactory in consideration of the fact that in commercial contracts a stipulated allowance comes into force only if a divergence of more than 0·2° C. from the guaranteed figure is observed. As *Dalican's* method has been made the basis of commercial transactions in this country, the United States, and France, new proposals for determining the "titer," however acceptable they may appear, have little chance of superseding the established method.

In view of the commercial importance of the correct determination of the "titer test," the question of a uniform method was laid before a Committee of the VIIth International Congress of Applied Chemistry, London (the author acting as president and reporter). *Frank Tate* described the apparatus used by him for the commercial determination of the "titer test." This apparatus is shown in Fig. 42, and was accompanied by the following description:—

a. A clear glass cylindrical vessel having an inside measurement 9 cm. high and 2·75 cm. diameter, and sides about 0·30 cm. thick, slightly rounded at the bottom, and provided at the top with a glass lip or ebonite flange.

b. An outer vessel of clear glass (13 cm. deep and 10 cm. wide), for the protection of the inner cylinder from draughts, etc.

c. An ebonite or wooden cover (not metal or other good conductor of heat), with a hole in the centre and slightly depressed flange on which to hang the flange of the inner cylinder.

d. Two small pins to keep the cylinder in position.

e. An accurate thermometer graduated from about −5° C. to about

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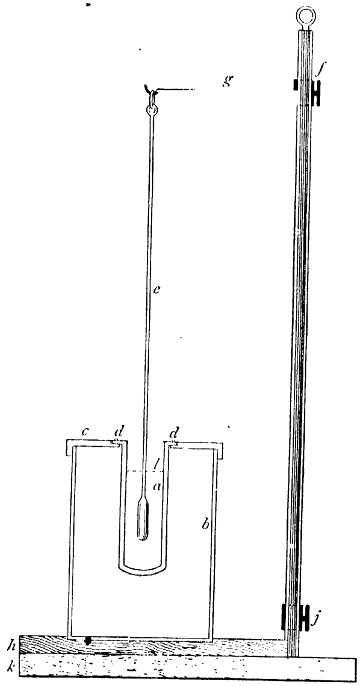
[1] *Chem. Zeit.*, 1901, 99.

70° C. in $\frac{1}{5}$ of a degree. The size of the bulb to be as nearly as possible 2·5 cm. in length and 0·60 cm. in diameter.

f. An upright pillar provided with :

g. An arm from which to suspend the thermometer, and fastened into :

h. A stout base or stand of wood, hollowed slightly to receive the larger glass vessel and keep it in position.



Quarter Size

Fig. 42.

For the convenience of raising the apparatus, if necessary, so as to bring the top of the mercury in the thermometer on a level with the eye, the apparatus may, if required, have the wooden stand attached to a sliding tube (*i*) fixed over the upright rod and movable by the screw (*j*). In this case there will be required a further foot (*k*) to support the whole.

The Committee agreed, since brokers, merchants, and others find it necessary for commercial purposes (such as tendering for sale, the removal of goods from quay, shipping, etc.) to have the "titer test" reported as quickly as possible, that in urgent cases the author's direction, viz. to allow the fatty acids to solidify and to stand over-night under a desiccator (see p. 501) need not be insisted upon, especially so, as *Frank Tate* urged that in his own experience no difference in results was obtained. Inasmuch as the author had found, not infrequently, that lower results were obtained when the fatty acids were tested immediately after they had been liberated, an experience which is confirmed also by other observers, the compromise arrived at by the decision of the Committee should be used in cases of urgency only.

The following table gives a list of "titer tests" collated from a very large number of observations made by the author :—

Titer Tests of Mixed Fatty Acids (Lewkowitsch)

Class of Oil.	Kind of Oil.	Titer Test. °C.	Remarks.
Drying oils	Linseed	20·6	
	Tung	37·2	
	Hemp seed	16·6	
	Safflower	16	
	Soya bean	21·2	
	Poppy seed	16·2	
Semi-drying oils	Cotton seed	32·0	Lowest
	" "	35·2	Highest
	Maize	19·0	
	Sesamé	23·8	
	Croton	19·0	
	Curcas	28·6	
	Rape	13·6	
Non-drying oils	Peach kernel	13·5	
	Almond	11·8	
	Arachis	29·2	
	Koëme	38·8	
	Olive	17·2	Lowest
	"	26·4	Highest
	Ben	37·8	
Marine animal oils	Japanese sardine	28·2	
	Cod liver	13·9	Lowest
	" "	24·3	Highest
	Seal	15·9	
	Whale	23·9	
Terrestrial animal oils.	Sheep's foot	21·1	
	Horses' foot	28·6	
	Neat's foot	26·5	

[TABLE

Titer Tests of Mixed Fatty Acids (Lewkowitsch)—continued

Class of Fat or Wax.	Kind of Fat or Wax.	Titer Test. °C.	Remarks.
Vegetable fats	Chaulmoogra oil	39·6	
	Pongam oil	44·4	
	Laurel oil	15·1	
	Carapa oil	34·9	
	Margosa oil	42·0	
	Niam fat	42·5	
	Mowrah seed oil	40·3	
	Palm oil, Bonny	35·9	
	,, Bassam	38·47	
	,, Lagos	43·925	
	,, Old Calabar	44·6	
	,, Salt Pond	44·475	
	,, New Calabar	45·55	
	,, Congo	45·05	
	Macassar oil	51·6	Lowest
	,, ,,	53·2	Highest
	Sawarri fat	47·0	
	Nutmeg butter	35·95	
	Shea butter	53·8	
	Cacao butter	48·3-49·6	
	Chinese vegetable tallow[1]	45·2	Lowest
	,, ,, ,,	53·1	Highest
	Palm nut oil	20·5	Lowest
	,, ,,	25·5	Highest
	Cocoa nut oil, commercial	22·55	Lowest
	,, ,,	25·2	Highest
	,, Cochin	25·2	
	Japan wax	59·4	
Animal fats	Horse fat	33·7	
	Horse marrow fat	38·55	
	Lard	42·0	
	Beef tallow, English	38·7	Lowest
	,, ,, ,,	45·1	Highest
	,, ,, North American	41·1	Lowest
	,, ,, ,, ,,	44·15	Highest
	,, ,, South American	42·95	Lowest
	,, ,, ,, ,,	46·25	Highest
	,, ,, Australian	38·3	Lowest
	,, ,, ,,	43·3	Highest
	Mutton tallow, English	41·5	Lowest
	,, ,, ,,	48·3	Highest
	,, ,, Australian	42·35	Lowest
	,, ,, ,,	48·05	Highest
	,, ,, New Zealand	45·9	Lowest
	,, ,, ,, ,,	48·0	Highest
	Beef marrow	38·0	
Liquid waxes	Sperm oil	11·9	
	Arctic sperm oil	8·6	

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[1] Commercial.

Refractive Index

The refractive indices of the mixed fatty acids supply no further information than is furnished by examining the oils and fats from which they have been derived, as all the differences observed in the refractometer can only depend on differences in the composition of the fatty acids. It has become customary of late, owing to the rapidity with which an observation is made, to record also the refractive indices of the fatty acids. The numbers so obtained are not collated here, as they will be found in Vol. II. Chap. XIV. in the tables of "Physical and Chemical Characteristics."

The following table may, however, be useful, as the refractive indices of the mixed fatty acids[1] are recorded side by side with the numbers observed for the corresponding oils and fats. There are also added a few isolated observations of butyro-refractometer numbers of liquid fatty acids (*Bömer*).

Refractive Indices of Fatty Acids

Kind of Oil.	Refractive Index at 60° C.		Butyro-refractometer "Degrees" at 40° C.
	of the Oil.	of the Mixed Fatty Acids.	of the Liquid Fatty Acids.
Linseed	1·4660	1·4546	
Poppy seed	1·4586	1·4506	
Sunflower	1·4611	1·4531	
Cotton seed	1·4570	1·4460	51·4-54·7
Sesamé	1·4561	1·4461	
Rape (crude)	1·4667	1·4491	
Castor	1·4636	1·4546	
Almond	1·4555	1·4461	
Arachis	1·4545	1·4461	
Olive	1·4548	1·4410	42·7
Cod liver	1·4621	1·4521	
Palm	1·4510	1·4441	
Cacao butter	1·4496	1·4420	
Palm nut	1·4431	1·4310	
Cocoa nut	1·4431	1·4295	
Lard	1·4410	1·4395	
,, (European)	...	...	42·8-44·2
,, (American)	...	...	43·1-44·7
Tallow (Beef)	1·4539	1·4375	
,, (Mutton)	1·4510	1·4374	
Butter	1·445-1·448	1·437-1·439	

W. B. Smith[2] endeavoured to calculate a factor for the conversion of the refractive index of oils and fats into that of their fatty acids. In view of the differences of natural oils and fats of one and the same species such factors must be more or less arbitrary.

With regard to the refractive indices of pure fatty acids and their glycerides, cp. also Vol. II. Chap. XIV. "Butter Fat." "Lard."

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[1] Thörner, *Journ. Soc. Chem. Ind.*, 1895, 43.

[2] *Journ. Ind. Eng. Chem.*, 1912, 36.

Rotatory Power

The optical rotation of fatty acids furnishes more valuable information than is obtained by examining the corresponding oils and fats polarimetrically, as the separation of admixed unsaponifiable matter from the isolated fatty acids permits to eliminate those adventitious substances which impart a slight rotation to many oils and fats. Thus the sesamé oil fatty acids, if freed from the (sitosterol and) sesamin, would exhibit no optical activity, as sesamé oil itself owes its optical activity to non-glyceridic substances. Should the optical activity of a glyceride be due to an asymmetric arrangement of the acid radicles in the molecule, the absence of optical activity in the mixed fatty acids would confirm in an unmistakable manner the view that one of the two antipodes of a racemic compound had been under observation.

In those cases, however, in which the optical activity is due to the configuration of the fatty acid molecule itself, the fatty acids, freed from foreign substances, would exhibit distinct optical rotation. Under this head fall ricinoleic acid, hydnocarpic acid, and chaulmoogric acid.

The following observations on the mixed fatty acids may be recorded :—

Mixed Fatty Acids of	Optical Rotation. $[\alpha]_D$.
Chaulmoogra oil	+52·6°
Hydnocarpus oil	+60·4°
Lukrabo oil	+53·6°
Oncoba oil[1]	+52·5°

It is probable that the mixed fatty acids of stillingia oil also exhibit optical activity (cp. Vol. II. Chap. XIV. "Stillingia Oil "). The fatty acids of rump gland wax are also stated to be optically active (see Vol. II. Chap. XIV. "Rump Gland Wax ").

Solubility

The mixed fatty acids of the majority of oils and fats are easily soluble in the usual organic solvents, and in addition thereto in absolute *alcohol*—in contradistinction to the oils (except castor oil) and fats themselves. The fatty acids of castor oil form an exception with regard to petroleum ether, inasmuch as they are insoluble in large quantities of the solvent, although they are miscible with an equal volume of petroleum ether. The fatty acids which form water soluble barium and magnesium salts (such as the volatile acids from butter fat and from cocoa nut oil and palm-kernel oil) can be resolved by petroleum ether into two fractions, soluble in petroleum ether and insoluble in petroleum ether[2] respectively.

The lower fatty acids (butyric, caproic, caprylic) being soluble in water (see Chap. III p. 110) are to the greatest part removed in the

[1] *Proc. Chem. Soc.*, 1913, 197.

[2] Cp. E. Ewers, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1910, xix. 529.

preparation of the mixed fatty acids from natural oils and fats (see Chap. III. p. 110).

The insoluble fatty acids from different oils and fats differ as regards solubility in *alcohol*. This may be gathered from the numbers recorded in the following table :—

Solubility of Mixed Fatty Acids in Absolute Alcohol

Mixed Fatty Acids from	100 Grms. of Absolute Alcohol dissolve at 0° C.	at 10° C.
	Grms.	Grms.
Mutton tallow	2·48	5·02
Beef tallow	2·51	6·05
Veal tallow	5·00	13·78
Lard	5·63	11·23
Butter fat	10·61	24·81

The differences in solubility are, however, not so pronounced that rules can be derived for the discrimination of various oils and fats. In some cases the different solubilities of fatty acids in dilute alcohol[1] may serve as a guide (cp. " Separation and Determination of Individual Saturated Fatty Acids," p. 552). The same strictures would apply to the employment of a mixture of alcohol and ether.[2]

The different solubility of the higher fatty acids in organic solvents, as compared with that (of the acids of low molecular weight and) of liquid fatty acids, respectively, affords means for the *approximate* separation of the several constituents of mixed fatty acids. This principle is made use of to isolate by means of alcohol at the ordinary temperature some high melting acids, such as arachidic acid (see below), and at very low temperatures to separate erucic acid from liquid fatty acids associated with it in rape oil.

The higher saturated fatty acids are more sparingly soluble in *petroleum ether* than the corresponding unsaturated acids, and require a higher temperature than the ordinary one for complete dissolution. On cooling, the higher saturated fatty acids separate out to some extent.

Fachini and Dorta[3] endeavoured to found on this behaviour a method of separating solid from liquid fatty acids (see p. 550) by working at temperatures of - 40 to - 45° C.

The solid saturated fatty acids are also more sparingly soluble in dry *acetone* than the unsaturated fatty acids having the same number of carbon atoms.

Hydroxylated acids, as a general rule, are insoluble in petroleum ether (see p. 579). Oxidised acids (p. 580) are likewise insoluble in petroleum ether, and may thereby be separated from the ordinary fatty acids. This procedure does not lead to satisfactory results in the case of a mixture of hydroxylated fatty acids, such as ricinoleic acid, with oleic acid (see p. 579). The principle of treating mixed fatty acids with a saturated solution of one specific acid was first introduced as a working process by *David* in the determination of stearic acid (see below).

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[1] Cp. Vandam, *Annal. de Pharm. de Louvain*, 1901, 201 ; *Analyst*, 1901, 320 ; H. S. Shrewsbury and A. W. Knapp, *Analyst*, 1910, 385.

[2] Dieterich, *Pharm. Centralh.*, 1896, No. 39.

[3] *L'Industria Saponiera*, 1910, 201.

The fatty acids of the liquid waxes behave like the acids of fatty oils (castor oil excepted). The fatty acids of the solid waxes, mostly representing, as they do, fatty acids of high molecular weight, are much more sparingly soluble in ether, petroleum ether, alcohol, etc., than are the acids of most oils and fats.

B. CHEMICAL METHODS

The chemical methods are arranged here in a logical system, so that the order of the description may serve at the same time as a guide in the technical examination of the mixed fatty acids. Further methods, involving a strictly scientific examination, will be described in Chapter XII. The subject-matter in this section will be treated under the following headings :—

1. Neutralisation Value—Mean Molecular Weight.
2. Lactones—Anhydrides.
3. Insoluble Fatty Acids.
4. Volatile Fatty Acids.
5. Separation of Insoluble Saturated from Unsaturated Fatty Acids.
6. Separation and Determination of Individual Solid Fatty Acids—Erucic Acid—Saturated Fatty Acids.
7. Determination of Oleic Acid in the absence of other Unsaturated Fatty Acids.
8. Detection, Separation, and Approximate Determination of Individual Liquid Fatty Acids—Oleic, Linolic, Linolenic, Clupanodonic.
9. Hydroxylated Fatty Acids.
10. Oxidised Fatty Acids.

1. Neutralisation Value—Mean Molecular Weight

The neutralisation value indicates the number of milligrams of potassium hydrate required to saturate one gram of the mixed fatty acids.

In the case of oils and fats having saponification values of about 195 and less, the mixed fatty acids obtained by the process described Chap. III. p. 110 may, for practical purposes, be considered as representing the total fatty acids contained in an oil or fat.

If, however, the saponification value of the sample exceed 200, the presence of considerable amounts of myristic (and) or lauric or of soluble acids must be suspected. It is advisable, indeed in most cases imperative, to remove the soluble acids (see below) and examine the mixed insoluble fatty acids.

The difficulties and inaccuracies involved in an endeavour to isolate the total fatty acids, *i.e.* both soluble and insoluble together—are such that in technical analyses such a method would become entirely impracticable.[1]

The determination of the neutralisation number is carried out in exactly the same manner as is described under the heading "Acid Value" (Chap. VI. p. 437). As a rule, about 5 grms. of the substance should be taken; smaller quantities should not be employed (if avoidable), as otherwise the errors of the method have too great an influence on the result.

The proposal[2] to weigh off 0·5 gram and titrate with decinormal potash obviously cannot yield satisfactory results and should be rejected: for a simple calculation will show that errors of 0·05 c.c. of deci-normal alkali seriously affect the correctness of the result. If only quantities smaller than 5 grams are available, then it is imperative to titrate with normal or half normal alkali until the point of saturation is nearly reached, and finish the titration with decinormal potash.

From the neutralisation number thus found, the mean molecular weight[3] of the fatty acids can be calculated as follows:—Let M be the molecular weight expressed in grams. Theory requires that M grms. be neutralised by 56·1 grams of potassium hydrate, KOH. Let n be the number of grams of potassium hydrate found by experiment to neutralise *one* gram of fatty acids, then we have the proportion

$$M : 56{\cdot}1 : : 1 : n \text{ ; hence, } M = \frac{56{\cdot}1}{n} \quad . \quad . \quad . \quad . \quad . \qquad (1).$$

In order to find n, the number of c.c. of normal KOH found for 1 grm. of fatty acid must be multiplied by 0·0561. If that number be a, then, evidently, we have

$$n = a \times 0{\cdot}0561 \quad . \quad . \quad . \quad . \qquad (2).$$

By substituting this expression in the above equation (1) we obtain

$$M = \frac{56{\cdot}1}{a \times 0{\cdot}0561} = \frac{1000}{a} \quad . \quad . \quad . \quad . \qquad (3).$$

In a similar manner the mean molecular weight of the isolated soluble acids (see below) can be determined.

In the following table I give the theoretical molecular weights and calculated neutralisation values of pure fatty acids; they will serve as a guide in the proper interpretation of such numbers as are obtained in the practical examination of the mixed fatty acids of a given oil, fat, or wax.

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[1] Cp. P. Simmich, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1911, xxi. 38.

[2] Juckenack and Pasternack, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, x. 99. Cp. W. Arnold, *Zeits. f. Unters- d. Nahrgs- u. Genussm.*, 1912, xxiii. 129.

[3] The determination of the molecular weight by cryoscopic and ebullioscopic methods can obviously only be applied in the case of pure acids.

Neutralisation Values of Fatty Acids

Acid.	Formula.	Molecular Weight.	Neutralisation Value. Mgrms KOH.
Acetic	$C_2H_4O_2$	60	935·0
Butyric	$C_4H_8O_2$	88	637·5
Caproic	$C_6H_{12}O_2$	116	483·6
Caprylic	$C_8H_{16}O_2$	144	389·6
Capric	$C_{10}H_{20}O_2$	172	326·2
Lauric	$C_{12}H_{24}O_2$	200	280·5
Myristic	$C_{14}H_{28}O_2$	228	246·1
Palmitic	$C_{16}H_{32}O_2$	256	219·1
Stearic	$C_{18}H_{36}O_2$	284	197·5
Oleic	$C_{18}H_{34}O_2$	282	198·9
Linolic	$C_{18}H_{32}O_2$	280	200·4
Hydnocarpic	$C_{16}H_{28}O_2$	252	222·6
Chaulmoogric	$C_{18}H_{32}O_2$	280	200·4
Linolenic	$C_{18}H_{30}O_2$	278	201·8
Clupanodonic	$C_{18}H_{28}O_2$	276	203·2
Ricinoleic	$C_{18}H_{34}O_3$	298	188·3
Arachidic	$C_{20}H_{40}O_2$	312	179·8
Gadoleic	$C_{20}H_{38}O_2$	310	181·0
Erucic	$C_{22}H_{42}O_2$	338	166·0
Cerotic	$C_{26}H_{52}O_2$	396	141·7
Melissic	$C_{30}H_{60}O_2$	452	124·1
Hydroxystearic	$C_{18}H_{36}O_3$	300	187·0
Dihydroxystearic	$C_{18}H_{36}O_4$	316	177·6
Trihydroxystearic	$C_{18}H_{36}O_5$	332	169·0
Sativic	$C_{18}H_{36}O_6$	348	161·2
Linusic	$C_{18}H_{36}O_8$	380	147·6
Dihydroxygadinic	$C_{20}H_{40}O_4$	344	163·1

In the following table the author has collated the neutralisation numbers and calculated mean molecular weights of the *insoluble* fatty acids of natural oils, fats, and waxes as obtained by the method of preparation described in Chapter III. p. 110.

The mean molecular weights of the mixed soluble acids of those oils and fats which have notable *Reichert* values will be given below.

For further details, the monographs of Vol. II. Chap. XIV. should be consulted.

[TABLE

Oils and Fats

Oil.	Class of Oil.	Group.	Neutralisation Number.	Mean Molec. Weight.
Perilla	Drying oils		197·7	284·0
Linseed			197	284·7
Tung			188·8	297·1
Stillingia			214·2	261·9
White acacia			200·1	280·4
Fir seed			193·0	290·6
Gynocardia			199·8	280·8
Safflower			199	281·9
Kaya			192·81	290·9
Echinops			192·6	291·5
Soya bean				
Poppy seed			199	281·9
Manihot			197·6	283·9
Sunflower			201·6	278·2
Yellow acacia			199	280·9
Para rubber tree seed			191·2	293·3
Raspberry seed			197·2	284·5
Hawthorn seed			202·9	276·4
Currant seed			211	265·9
Blackberry seed			199·7	280·9
Clover, red	Semi-drying oils	Cotton seed oil group	198·1	283·2
Clover, white			197·6	283·8
Grape seed			187·4	299·3
Pumpkin seed			197	284·7
Water melon			197·1	284·1
Maize [corn]			198·4	282·7
Persimmon seed			192·7	291·5
Kapok			191	293·7
Cotton seed			202-208	277·7-269·7
Sesamé			200·4	279·9
Croton			201	279·1
Zachun			200	278·2
Tomato seed			199·5	281·2
Spindle tree		?	223·6	250·9
Garden cress		Rape oil group	193·2	290·3
Rape			185·0	303·2
Black mustard seed			187·1	300-299·8
White mustard seed			185·8	302-301·9
Radish seed			189·5	296
Jamba			173·9-183·9	322·6-305

Oils and Fats—continued

Oil or Fat.	Class of Oil or Fat.	Group.	Neutralisation Number.	Mean Molec. Weight.
Small fennel	Non-drying oils		197·6	283·9
Cherry kernel			189	296·8
Apricot kernel			194	289·1
Plum kernel			200·5	279·8
Peach kernel			200·9	279·2
Almond			204	275·0
Sanguinella			195·1	287·5
Arachis			201·6	278·2
Rice			193·9	289·3
Tea seed			195·0	287·6
Tsubaki			197	284
Sasanqua			199·6	281
Hazel nut			200·6	279·6
Elderberry			204·8	273·9
Staff tree			188·7	296·5
Olive			200	280
Calophyllum			194	289·2
Coffee berry			175	320·5
Canari			191-201	278·6
Castor		Castor oil group	192·1	292·0
Herring	Marine animal oils	Fish oils	192·2	291·9
Stickleback			181·5	309·0
Cod liver		Liver oils	204-207	275·0-271·0
Tunny fish			177·0	316·9
Seal		Blubber oils	193·2	290·3
Turtle			209·3	268
Brown fish			207	271·0
Chrysalis	Terrestrial animal oils		199·34	281·43
Egg			194·9	287·8
Neat's foot			203	276·3
Chaulmoogra	Vegetable fats	Chaulmoogra oil group	215	260·9
Hydnocarpus			214	262·1
Lukrabo			202·5	277·0
Nux vomica			199·5	281·2
Baobab			197·5	284·1
Niam			198·1	283·7
Njave			201·7	284·6
Aouara		Palm oil group	199·1	281
Palm			205·6	272·8
Akee			207·7	270·1
Macassar			191·6	292·7
Sawarri			205·6	272·8
Mafura tallow			194·3	288·7

Oils and Fats—continued

Oil or Fat.	Class of Fat.	Group.	Neutralisation Number.	Mean Molec. Weight.
Ochoco		Myristica group	252·8	221·9
Surin		Cacao butter group	196·9	284·9
Rambutan tallow			186·4	300·9
Cacao butter			190	295·2
Chinese vegetable tallow			182-208	308·2-269·7
Kokum butter			198·9	282·0
Borneo tallow			205·5-197·5	273-284
Mocaya		Cocoa nut oil group	254	220·8
Aouara kernel			249·1	225
Palm nut			252-264	211-223
Cocoa nut			258-266	210-217
Cáy-Cáy		Dika fat group	253	222
Kusu			292·8	191·6
Japan wax			213·7	262·5
Myrtle wax			230·9	242·9
Blackcock	Animal fats	Semi-drying fats	199·3	281·4
Lynx			202·7	276·8
Marmot			209·6	267·7
Horse			202·6	276·9
Hare			209·0	268·4
Rabbit (wild)			209·5	267·7
Rabbit (tame)		Non-drying fats	218·1	257·2
Horse marrow			210·8-217·6	266·1-257·8
Goose (domestic)			202·4	277·1
Goose (wild)			196·4	285·6
Chicken			200·8	279·3
Lard			201·8	278·0
Wild boar			203·6	275·5
Dog			199·2	281·6
Wild cat			203·8	275·2
Beef marrow			204·5	274·3
Bone			200	280·5
Beef tallow			198	283·3
Mutton tallow				
Elk			201·4	278·5
Roebuck			200·5	279·8
Fallow buck			201·4	278·5
Stag			201·3	278·6
Butter		Milk fats	210-220	267·1-255·0

Waxes

Wax.	Class of Wax.	Group.	Neutralisation Number.	Mean Molec. Weight.
Sperm	Liquid Waxes		199·6-190·8	281-294
Wool wax . . .	Solid Waxes	Animal Wax	171·3	327·5

2. Lactones—Anhydrides

It has been stated already that, as a rule, the amount of unsaponifiable matter in oils and fats may be neglected in the determination of the neutralisation number of the fatty acids. Hence, if the fatty acids, instead of being titrated with aqueous alkali in the cold, were boiled with an excess of alcoholic potash (see " Saponification Value," Chap. VI. p. 379), the same number of milligrams of potassium hydrate should be found, provided the amount of unsaponifiable matter be negligible. In other words, the neutralisation and saponification values of fatty acids should be identical. In case, however, the fatty acids contain such substances as lactones, or anhydrides of the fatty acids, which do not combine with aqueous alkali in the cold (and are only hydrolysed on boiling with alcoholic potash) then the saponification value of the fatty acids will be higher than the neutralisation number *Tortelli and Pergami*[1] state that this holds good for all fatty acids, with the exception of stearic acid. Their results are reproduced in the following table :—

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[1] *L'Orosi*, 1901, 1.

[Table

Pure Fatty Acids.	I. Neutralisation Value.	II. Molecular Weight calculated from I.	III. Saponification Value.	IV. Molecular Weight calculated from III.	V. Difference, II.-IV.
Palmitic	202·7	276·5	218·7	256·4	20·1 (!!)
Stearic	198·7	282·3	198·9	282·0	0·3
Arachidic	163·9	342·3	170·1	329·8	12·5
Oleic, freshly prepared from olive oil	199·5	281·2	201·4	278·5	2·7
Oleic, 2 years old, from beef fat	191·0	293·8	202·8	276·6	17·2
Oleic, commercial, several years old	181·6	308·2	189·3	296·5	11·7
Mixed Fatty Acids from					
Linseed oil, fresh	194·6	288·2	201·8	277·9	10·3
,, ,, 3 years old	191·5	292·8	205·4	273·2	19·6
Sunflower oil, fresh	193·4	290·0	201·5	278·4	11·6
,, ,, 2 years old	194·5	287·6	199·6	281·0	7·6
Nut oil, fresh	200·2	279·7	202·8	276·3	3·4
Nut oil, same, kept in the dark 1 month	200·5	279·8	200·8	279·3	0·5
Nut oil, same, kept in the dark 2 months	196·0	286·2	208·5	269·0	17·2
Cotton seed oil, fresh	200·9	279·2	203·1	276·2	3·0
,, ,, 2½ years old	194·3	288·7	204·5	274·3	14·4
Ravison oil, fresh	176·8	317·3	183·2	306·2	11·1
,, ,, 2 years old	178·8	313·7	182·1	308·0	5·7
Rape oil, fresh	176·6	317·7	181·2	309·6	8·1
,, ,, 2 years old	178·3	314·6	182·5	307·4	7·2
,, ,, 5 years old	176·1	318·8	181·4	309·1	9·1
Castor oil, fresh	187·0	300·0	191·0	294·3	5·7
,, ,, 2½ years old	183·1	306·4	189·0	296·7	9·7
Cherry kernel oil	191·3	293·2	213·7	262·5	31·7
Apricot kernel oil, fresh	199·5	281·2	200·2	280·1	1·1
Apricot kernel oil, acids remained 1 month in the dark	196·0	286·2	199·1	281·7	4·5
Apricot kernel oil, acids remained 2 months in the dark	197·4	284·2	198·2	283·0	1·2
Apricot kernel oil, acids remained 5 months in the dark	187·0	300·0	200·0	280·5	19·5
Apricot kernel oil, 2 years old	196·8	285·0	200·0	280·5	4·5
Apricot kernel oil, same acids exposed to light 1 month	182·9	306·0	194·1	288·9	17·1
Almond oil, fresh	195·8	286·5	200·3	278·3	8·2
,, ,, 2½ years old	196·0	286·2	202·2	277·5	8·7
Arachis oil, fresh	195·2	287·3	200·2	280·2	7·1
,, ,, 2½ years old	195·5	286·9	200·0	280·5	6·4
Hazelnut oil, fresh	197·6	283·8	199·7	280·9	2·9
Olive oil, 3 years old	194·5	288·4	200·9	279·1	9·3
Vegetable tallow, 3 years old	213·8	262·2	214·0	262·1	0·1
Vegetable tallow, acids exposed to light for 9 months	204·2	274·7	215·7	260·0	14·7
Lard, fresh	205·0	273·4	204·8	273·9	0·5
,, 2½ years old	203·4	275·8	203·1	276·2	0·4
Beef tallow, fresh	205·7	272·7	209·9	267·2	5·5
,, ,, 2 years old	205·4	273·1	207·1	270·8	2·3

The author has, however, shown[1] that it would be premature to accept this general statement, as in a number of cases he obtained figures which contradict *Tortelli and Pergami's* views. In some cases the numbers found agree with those given by *Tortelli and Pergami*, in other cases the differences are so small that they fall within the errors of the method. Even negative differences were obtained, as will be seen from the following table, in which I collate some results ascertained in my laboratory :—

Neutralisation and Saponification Values of Mixed Fatty Acids[2]
(*Lewkowitsch*)

Acid from	I. Neutralisation Value.	II. Molecular Weight calculated from I.	III. Saponification Value.	IV. Molecular Weight calculated from III.	V. Difference, II.-IV.
Linseed oil	201·8	278·0	199·8	280·9	− 2·9
,, ,, ...	194·7	288·1	199·8	280·7	+ 7·4
,, ,, ...	195·2	287·1	199·0	281·9	+ 5·5
Tung oil	181·25	309·5	198·7	282·3	+27·2
Stillingia oil . . .	206·3	271·9	210·5	266·5	+ 5·4
Nut oil	201·2	278·9	199·5	281·3	− 2·4
Safflower oil . . .	200·3	280·1	199·7	280·9	− 0·7
Maize oil	197·1	284·6	199·8	280·7	+ 3·9
Cotton seed oil . . .	197·4	281·1	204·2	274·7	+ 9·4
,, ,, ...	200·5	279·8	205·2	273·3	+ 6·5
,, ,, ...	201·9	277·8	205·1	273·5	+ 4·3
Rape oil	182·3	307·7	184·9	303·3	+ 4·4
Croton oil	197·3	281·3	203·3	275·9	+ 8·4
Castor oil	176·9	317·1	177·2	316·5	+ 0·6
,, ,, ...	175·7	319·3	177·8	315·5	+ 3·8
,, ,, ...	174·7	321·1	176·5	317·8	+ 3·3
Apricot kernel oil . .	198·0	283·3	202·0	277·7	+ 5·6
,, ,, (California)	197·8	283·6	202·8	276·6	+ 7·0
,, ,, ...	194·0	289·1	200·7	279·5	+ 9·6
Peach kernel oil . . .	196·8	285·0	205·0	273·6	+11·4
Almond (sweet) oil . .	196·4	285·6	201·7	278·1	+ 7·5
,, (Sicily) . . .	198·8	282·1	202·2	277·4	+ 4·7
,, (Mazagan bitter) .	196·8	285·0	203·1	276·2	+ 8·8
,, (small Indian) .	195·8	286·5	200·7	279·5	+ 7·0
,, (Mogador bitter) .	197·1	284·6	203·2	276·0	+ 8·6
,, ...	207·8	269·9	207·6	270·2	− 0·3
Olive oil	200·5	279·8	201·9	277·8	+ 2·0
,, ,, ...	200·9	279·2	200·9	279·2	0·0
Palm oil	206·2	272·0	206·9	271·1	+ 0·9
,, ,, ...	205·5	272·9	206·3	271·9	+ 1·0
Cocoa nut oil . . .	271·6	206·5	271·0	207·0	− 0·5
,, ,, . . .	271·5	206·6	270·6	207·3	− 0·7
Lard	196·0	286·2	205·1	273·5	+12·7
,, ...	196·2	285·9	204·5	274·3	+11·6
Margosa oil . . .	194·1	289·0	198·9	282·0	+ 7·0
Pongam oil. . . .	192·5	291·4	195·8	286·5	+ 4·9
Oleic acid (iodine value 81·6)	201·2	278·8	201·4	278·5	+ 0·3

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[1] Lewkowitsch, *Jahrbuch der Chemie*, 1901, xi., 359.

[2] Cp. also "Water-melon Oil" and "Datura Oil," Vol. II. Chap. XIV.

Tortelli and Pergami's statement that the difference between the saponification and neutralisation values of mixed fatty acids increases with the age of the sample, finds its explanation in the fact that such fatty acids as a rule contain small amounts of volatile and of oxidised fatty acids. Hence in the case of old oils, especially fish, liver, and blubber oils, the differences between saponification and neutralisation are considerable (see Vol. II. "Marine Animal Oils").

Differences between the saponification and neutralisation values may also be due to the formation of anhydrides of the fatty acids themselves on heating; in many cases a notable difference would point to the presence of inner anhydrides or lactones, the occurrence of which in natural fats (Vol. II. Chap. XIV. "Sawarri Fat") and in wool wax was first proved by *Lewkowitsch.*[1] Thus wool wax fatty acids are easily converted, to some extent, into inner anhydrides on heating to 100° C. (cp. Chap. XI., and Vol. II. Chap. XIV.).

Hydroxylated fatty acids especially are likely to suffer dehydration with the formation of inner anhydrides. Thus the fatty acids of castor oil readily form inner anhydrides (polymerisation products); indeed it has been shown that the fatty acids of castor oil become "polymerised" even at the ordinary temperature on prolonged keeping, forming polyricinoleic acids (see Chap. III. p. 214). In the case of such polymerised ricinoleic acids the difference is considerable [2] between the saponification and the neutralisation values. Another example of this kind is furnished by stearolactone, the inner anhydride of γ-hydroxystearic acid (see Chap. III. p. 226).

The proportion of lactones and other anhydrides may be determined either volumetrically or gravimetrically.

(a) *Volumetric Determination of Lactones (Anhydrides)*

Five grams of the sample are weighed off, dissolved in neutralised alcohol, and titrated with aqueous alkali in the cold. (It should be noted that the aqueous solution at the end of the titration must contain at least 50 per cent of alcohol, so as to prevent hydrolysis of soap.) Thus the neutralisation value of the sample is found. In a second experiment 1·5 to 2·0 grms. are boiled with alcoholic potash exactly as described under "Saponification Value" (Chap. VI. p. 379) and titrated. Thus the saponification value is found.

The difference between the saponification and neutralisation values furnishes a measure of the lactones present. If the chemical composition of the lactone be known, its quantity can be calculated as shown by the following example:—

The saponification value of a mixture of fatty acids and stearoactone was found to be 194·3, and its neutralisation number 153·9.

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[1] *Proc. Chem. Soc.*, 1889, 69; *Journ. Soc. Chem. Ind.*, 1890, 844; 1892, 39; 1896, 14.

[2] Cp. Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1893, 67.

The difference, $194{\cdot}3 - 153{\cdot}9 = 40{\cdot}4$, corresponds to the amount of stearolactone present. As the saponification value of stearolactone is 198·9, calculated from the proportion :—

$$282 : 56100 : : 1 : x ; \; x = 198{\cdot}9,$$

the percentage of stearolactone is found from the following proportion:—

$$198{\cdot}9 : 100 : : 40{\cdot}4 : x ; \; x = 20{\cdot}3 \text{ per cent.}$$

As the nature of the lactones (or anhydrides) occurring in a sample submitted to an analyst is but rarely known, it will be found preferable to isolate the lactone and determine it quantitatively, as described in the following process, which permits at the same time to determine the free fatty acids volumetrically.

(*b*) *Gravimetric Determination of Lactones* (*Anhydrides*)

Five grams, or more, of the sample are dissolved in neutralised alcohol, and titrated with aqueous caustic potash in exactly the same manner as described above under "Neutralisation Value." The lactone or anhydride remains unaffected as long as free fatty acid is present. The soap solution is then shaken out with ether or petroleum ether (see "Unsaponifiable Matter," Chap. VI. p. 455), care being taken not to dilute the soap solution too much so as to cause dissociation of the soap, when acid soaps may pass into the ethereal solution). The ethereal solution is then filtered off, the ether evaporated off, and the residue weighed. The residue must be free from ash ; its neutralisation value should, of course, be *nil*.

If a further examination of the isolated lactone (or anhydride) be desired, its saponification value, iodine value, etc., may be determined.

3. Insoluble Fatty Acids

(*a*) *In Oils and Fats*

It has been repeatedly pointed out that the fatty acids as prepared from oils and fats by the method described in Chapter III. contain, in the majority of cases, negligible quantities of unsaponifiable matter, and it has also been explained that if the saponification value of an oil or fat does not exceed 195, soluble or volatile acids are absent, or only present in negligible quantities. It has further been stated that in case the saponification value be higher than 200, the presence of glycerides containing soluble or volatile acids or considerable quantities of lauric (and) or myristic acid may be taken as granted.

The proportion of insoluble fatty acids in oils and fats had for some time been looked upon as a "characteristic" number (and even as a "constant") and was described as such in former editions of this work under the term "Hehner Value," although it had been emphasized that the isolated insoluble fatty acids contained varying amounts of unsaponifiable matter. In the present work the proportion of fatty matter obtained by the method given in Chap. III. p. 110, will be recorded under the heading :—*Insoluble fatty acids + unsaponifiable matter*, in the tables of "Characteristics of Insoluble Fatty Acids" (see Vol. II. Chap. XIV.).

The amount of fatty acids obtainable from a soap by decomposition with a mineral acid had been determined quantitatively as far back as the eighteenth century by *Geoffrey* and *Macquer*, but they still looked upon the fatty acids as the original fat used in making the soap—a procedure which in some modified form still survives at the present day in Marseilles, where soaps are branded (and sold) with the percentage of *fat* corresponding to the amount of fatty acids actually contained in the soaps.

The usual method for determining the amount of insoluble fatty acids in fats and oils in its first stages is essentially that described in Chap. III. p. 110, smaller quantities than 50 grms. being used and certain precautions being observed which are detailed in the following lines. It has been pointed out already that the volatile soluble acids are to the largest extent removed with the wash waters.

A quantitative method for determining the proportion of insoluble fatty acids in oils and fats containing volatile (soluble) acids was proposed by *Angell and Hehner*[1] for the examination of butter fat and the detection of foreign fats therein. At first they used aqueous potash for saponification, which naturally caused great difficulties; hence the process became only workable through the introduction of alcoholic potash (proposed for this purpose by *Turner*). The determination is carried out in the following manner :—3-4 grams of fat are saponified as described under "Saponification Value" (Chap. VI. p. 379). The alcoholic solution is then rinsed with boiling water into a porcelain dish of about 5 inches diameter, and boiled down on the water-bath to pastiness. The soap is dissolved in 100-150 c.c. of water, and acidified with dilute sulphuric acid. The contents of the dish are then heated, until the liberated fatty acids float on the top as a clear oily layer. This is brought on to a filter paper of about 4-5 inches diameter, previously dried at 100° C. and accurately weighed in a weighing bottle or small beaker (covered with a watch-glass). The filter-paper should be of stout material, as ordinary filtering paper readily allows the liquid to run through turbid. A good plan to prevent this is to have the filter half full of hot water, before the fatty matter is transferred to it, and to keep it full till all the liquid is added. Finally, the fatty acids are washed on the filter with boiling water until a few c.c. of the wash-water do not redden sensitive tincture of litmus. (For 3 grms. of butter fat no less than 2000 to 3000 c.c. of wash-water are required.) The funnel with the filter is then immersed in a vessel of cold water, so that the water outside and the acids inside are at the same level. The water is then allowed to drain off, the filter is transferred to the beaker in which it had previously been weighed, is dried at 100° C.

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[1] *Butter: Its Analysis and Adulterations*, London, 1874.

for two hours, and weighed. The fatty matter is dried for another hour or an hour and a half, and weighed again. The difference between the two weights will, as a rule, be below 1 mgrm.

In case the oil or fat under examination contains readily oxidisable fatty acids such as linolic, linolenic, clupanodonic acid, it is necessary to carry out the operations with exclusion of air as much as possible. The bulk of the alcohol is, therefore, evaporated off from the soap solution contained in the flask in which the saponification has been carried out, and the soap is then decomposed in the flask. The fatty acids are washed on the filter with as little exposure to the air as possible, the filter being kept covered with a watch glass. The washed fatty acids are then rinsed with dry ether into a tared flask, and the solvent is evaporated off in a current of hydrogen or carbon dioxide. This *modus operandi* does away with the drying and weighing of a tared filter.

Strictly concordant results are not obtainable by this method, as it entails a number of inherent errors, detailed consideration of which is required in each special case.

Taking the final operation first, there are two sources of error—one causing an increase, the other a decrease in weight. To a certain extent, however, one error is compensated by the other. On the one hand unsaturated acids may become oxidised, whilst on the other hand loss is incurred through volatilisation of fatty acids.[1]

The following table, due to *Tatlock*,[2] gives some indications as to the amount of error caused by drying fatty acids at 90° C. :—

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[1] Fahrion (*Chem. Zeit.*, 1907, 437) observed the formation of neutral substances, and conjectured that polymerisation products are formed and not anhydrides, as he was unable to detect oleic anhydride on heating oleic acid with dehydrated copper sulphate on the water-bath.

[2] *Journ. Soc. Chem. Ind.*, 1890, 374. Cp. Fendler and Frank, *Zeits. f. angew. Chem.*, 1909, 254.

Table showing Loss (or Gain) in Weight of Dry Fatty Acids, during different Periods, at 90° C.

Time heated at 90° C.	Fatty Acids from								Stearic Acid.	Olive Oil containing 9·42 per cent Free Oleic Acid.	Olive Oil from which Free Fatty Acid was removed.
	Olive Oil (1).	Olive Oil (2).	Olive Oil (3).	Olive Oil (4).	Castor Oil.	Rape Oil.	Cotton Seed Oil.	Linseed Oil.			
Dry.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.	100·00.
24 hours . .	99·22	99·33	99·18	99·50	99·18	100·50	99·26	101·25	100·08	100·24	100·88
48 ,, . .	98·88	98·92	98·85	99·06	98·51	100·30	99·04	101·23	100·06	100·52	101·42
72 ,, . .	...	...	...	98·70	97·85	99·89	...	...	99·72	100·52	101·32
96 ,, . .	98·18	98·20	98·17	...	...	...	98·12	100·42	...	...	...
120 ,, . .	...	...	...	98·09	96·82	99·46	97·87	100·19	98·22	100·10	100·36
192 ,, . .	96·96	97·08	96·97								
360 ,, . .	95·45	95·50	95·42								
528 ,, . .	94·14	94·17	94·10								
720 ,, . .	92·62	92·67	92·57								

In the case of oleic acid *Fahrion*[1] ascertained the following respective losses on drying for six hours at 110° C., 120° C., and 115° C.:—2·8 per cent, 5·2 per cent, and 3·2 per cent.

In order to obviate losses of fatty acids *Lechartier* (in 1880) and *J. West Knight*[2] proposed the following method, which is based, on the one hand, on the insolubility in water of the barium salts of the higher fatty acids, and, on the other, on the ready solubility of the barium salts of the volatile acids:[3]—1-3 grms. of the oil or fat are saponified with alcoholic potash in the usual manner; the solution is then made up with cold distilled water to 300 c.c., and an aqueous solution of barium chloride added until no further precipitation takes place. The precipitate is collected on a filter, washed with warm water, and transferred to a separating funnel, in which the barium salts are decomposed with hydrochloric acid.[4] The liberated fatty acids are dissolved in ether, the ethereal solution is washed and run into a weighed flask; after distilling off the ether, the residue is dried and weighed.

Inasmuch as the solubility of the lower fatty acids does not necessarily correspond to the solubility of their barium salts, it is open to doubt whether the results obtained by this method agree with those found by the method described above. In the case of butter fat for which this *modus operandi* was proposed, the numbers published by *Knight* agree closely with those obtained by the foregoing method.[5]

Other errors, which in more pronounced degree render the quantitative determination uncertain, are the varying proportions of unsaponifiable matter and the presence of glycerides containing lauric acid. Although the proportion of unsaponifiable matter is negligible in most cases, it may in others lead to serious errors. Thus, to take an example, the amount of *insoluble fatty acids + unsaponifiable matter* in "Nux vomica fat" was found to be 95·2 per cent, and this number might have been interpreted as pointing to a normal amount of fatty acids of the mean molecular weight of about 276. On closer investigation it was, however, found that the unsaponifiable matter amounted to as much as 12·2 per cent. Hence the proportion of insoluble fatty acids actually amounted to only 83 per cent (95·2-12·2). Similar cases are recorded in the monographs of Vol. II. Chap. XIV. It is therefore evident that the weighed fatty matter can only be looked upon as consisting of insoluble fatty acids with a negligible quantity of unsaponifiable matter, if further examination warrants such a conclusion; for only in the case of pure triglycerides will the weight of the fatty matter be identical with the percentage of insoluble fatty acids.

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[1] *Chem. Zeit.*, 1907, 437.

[2] *Analyst*, 1881, 155.

[3] Barium salts were first prepared by Chevreul.

[4] It is not admissible to dry the salts, weigh them, incinerate, and derive the weight of the fatty acids from the difference of the first weight and the amount of baryta in the ash (cp. Chap. III. "Stearic Acid," p. 165). Nor is it advisable to employ the soda or potash salts as suggested by Fahrion, *Chem. Zeit.*, 1906, 267; 1907, 437. Hence methods based on the determination of the weight of the potash salts obtainable from the total fatty acids although so frequently proposed, must be rejected.

[5] Asbóth states that the lead salts of the volatile acids are also soluble in water; but his statement must be accepted with reserve as his paper does not furnish any proof for this assertion.

Since the theoretical yields of insoluble fatty acids obtainable from their monoglycerides, diglycerides, and triglycerides furnish useful indications in the examination of oils and fats, the author collates the theoretical numbers in the following table:—

Percentages of Insoluble Fatty Acids in Mono-, Di-, and Tri-glycerides (Lewkowitsch)

Glyceride of Acid.	Monoglyceride.	Diglyceride.	Triglyceride.
Acetic	0	0	0
Butyric	0	0	0
Valeric	0	0	0
Caproic	0	0	0
Caprylic	–	–	–
Capric	–	–	–
Lauric	–	–	–
Myristic	75·50	89·05	94·75
Palmitic	77·58	90·15	95·29
Stearic	79·33	91·02	95·73
Oleic	79·22	90·95	95·70
Linolic	79·10	90·90	95·67
Linolenic	78·98	90·83	95·63
Clupanodonic	78·86	90·79	95·61
Ricinoleic	80·12	91·43	95·93
Arachidic	80·82	91·76	96·09
Erucic	82·04	92·35	96·39
Cerotic	84·26	93·40	96·90
Melissic	85·93	96·17	92·27
Hydroxystearic	80·2	91·47	95·95
Dihydroxystearic	81·02	91·87	96·15
Trihydroxystearic	81·78	92·23	96·35
Sativic	82·48	92·56	96·50
Linusic	83·70	93·15	96·77
Mixed Triglycerides—			
Myristopalmitoölein	...	...	95·3
Oleodipalmitin	...	...	95·3
Stearodipalmitin	...	...	95·44
Oleopalmitostearin	...	...	95·58
Palmitodistearin	...	...	95·59
Oleodistearin	...	...	95·62
Elaïdodistearin	...	...	95·62

Against the glycerides of easily soluble fatty acids I have placed a 0, and in the case of the intermediate fatty acids, which require very large quantities of water for solution, I have placed a – in order to express thereby that no definitive figure can be given. By using a very much larger amount of boiling water than directed above, the total content of caproic, caprylic, and capric acids can be washed out. If, however, lauric acid is a preponderant constituent of the mixed fatty acids, it would be practically impossible to remove it by washing. Hence, in the case of those fats which contain notable amounts of lauric acid, the uncertainty of knowing when the washing should be stopped offers an insurmountable difficulty. To this very uncertainty must be attributed the fact that widely differing numbers have been recorded for the proportion of insoluble fatty acids + unsaponifiable in cocoa nut and palm nut oils.

A still more striking example is afforded by "Kusu Oil" (see Vol. II. Chap. XIV.), which yielded with 2000 c.c. of boiling water for 3-4 grams of fat—81·8 per cent of insoluble acids + unsaponifiable. There can be no doubt that further washing would have brought down this number considerably, in direct proportion to the further amount of hot water used. By persistently continuing the operation, the proportion of insoluble acids + unsaponifiable would have tended to approach *zero*, as kusu oil practically consists of laurin (the theoretical saponification value of which is 263·8), probably in admixture with a small quantity of lower glycerides (cp. also Vol. II. Chap. XIV. "Tangkallak Fat").

In order to complete the information obtained by weighing the insoluble fatty acids, it is advisable to ascertain their mean molecular weight (cp. p. 512 and Vol. II. Chap. XIV. "Butter Fat"). A glance at the numbers given in the last column of the preceding table shows that the differences between the numbers for palmitin, stearin, olein, linolin, linolenin, and ricinolein are so small that they fall within the errors of the gravimetric method. Hence, in these cases the discriminative value of the percentage number would appear to be *nil.* It only acquires importance when a mixture of glycerides of higher fatty acids with glycerides of fatty acids lower than myristic acid is under examination. In that case the proportion of insoluble fatty acids + unsaponifiable will be below 95, provided notable amounts of unsaponifiable matter be absent, and it will then be possible to derive from the difference between 95 and the number actually found a measure of the amount of glycerides of lower fatty acids in a natural product.

The percentage number of the insoluble fatty acids indicates in a direct manner what can be derived implicitly from the saponification value if exceeding 200, or from the *Reichert-Meissl* value if exceeding 5 (cp. "*Reichert-Meissl* Value," table, p. 423). Hence the determination of the percentage number has been almost completely superseded by that of the saponification and *Reichert* values.

The percentage numbers of the majority of oils and fats lie in the neighbourhood of 95. Those oils and fats which notably deviate from this number are enumerated in the following table:—

Oil or Fat.	Insoluble Acids + Unsaponifiable.
Croton	89·0
Small fennel	88·8
Elderberry	91·75
Senega root	85·8
Shark liver	86·9 (?)

Oil or Fat.	Insoluble Acids +Unsaponifiable.
Dolphin body	93·07
Dolphin jaw	66·3
Porpoise body	91·04
Porpoise jaw	70·2
Brown fish	85·5
Laurel	83·5-86·8
Carapa	93
Akee	93
Macassar	91·5
Maripa	88·88
Aouara kernel	91·7
Palm nut	87·6-91·1
Cocoa nut	82·4-90
Japan wax	90·6
Tangkallak	76 [1]
Kusu	81·8 [1]
Butter	86·5-90·1

It will be seen that, with the exception of Japan wax, the same oils and fats occur in the table of *Reichert* and *Reichert-Meissl* values. The occurrence of dibasic acids in Japan wax explains the low number.

(*b*) *In Waxes*

The fatty matter obtained on saponifying waxes and decomposing the resulting product with mineral acid contains both fatty acids and alcohols; [2] as the latter are insoluble in water, the percentage number found exceeds 100, water having been assimilated during the saponification. Hence the determination of the percentage number alone would furnish entirely useless results.

In case it be desired to weigh the amount of insoluble fatty acids in waxes, the fatty matter obtained on saponification must first be freed from the alcohols [2] (cp. p. 455). The following table contains the proportions of insoluble fatty acids in some waxes, as ascertained in the author's laboratory :—

Percentage Numbers of Fatty Acids in Waxes (*Lewkowitsch*)

Sperm oil	60-64
Arctic sperm oil	61-65
Carnaüba wax	47·95
Wool wax	59·8
Beeswax	46·77
Spermaceti	53·45
Insect wax	51·54

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[1] These numbers may be still too high.

[2] Any hydrocarbons present would be found with the alcohols.

4. Volatile Fatty Acids

SOLUBLE VOLATILE ACIDS AND INSOLUBLE VOLATILE ACIDS

If the saponification value of an oil or fat exceeds considerably 200, and if, subsequently, a notable *Reichert-Meissl* value has been found, the presence of volatile fatty acids is proven. It has been shown above (p. 416) that the earlier attempts to estimate the amount of total volatile acids have not been attended with success, and that the *Reichert* method is only a conventional one. Since in the *Reichert* test only a portion of the volatile fatty acids is obtained, the further examination of the distillate and the isolation of the individual volatile fatty acids contained therein will not furnish complete information (see Chap. XII.) as to the total amount and the nature of the volatile fatty acids.

The volatile fatty acids must not be considered as being identical with the soluble acids, although the bulk of the volatile acids in most oils and fats characterised by high *Reichert* values are "soluble" in water. Since the occurrence (in Japan wax) of soluble dibasic acids—which are non-volatile—has been demonstrated, it is necessary to exercise due circumspection.

If the total amount of volatile acids only is required, they may be obtained in substance by a method similar to the one proposed by *Lewkowitsch* for the determination of the acetyl value, which consists in distilling off the total amount of volatile fatty acids exactly as described for the determination of the acetic acid in the "distillation process." This method differs, of course, from the *Reichert* process in that the *total amount* of volatile fatty acids is driven off. Six to seven hundred c.c. of water are distilled over, and the distillate is titrated with decinormal potash, using phenolphthalein as an indicator. The number thus found is calculated to 1 grm. of oil or fat.

The following table contains the total volatile acids furnished by some commercial oils and fats.[1] A few numbers have been ascertained by the "Filtration Process."

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[1] Lewkowitsch, *Analyst*, 1899, 319. A much more elaborate method proposing to distil off the volatile acids *in vacuo* is proposed by E. Welde, *Biochem. Zeits.*, 1910 (28), 504; cp. also A. Bruno, *Annal. de chimie analyt.*, 1911 (16), 138.

Volatile Acids in Commercial Oils and Fats (Lewkowitsch)

Kind of Oil or Fat.	Total Volatile Fatty Acids per gram ; in terms of Mgrms. KOH.	
	Distillation Process.	Filtration Process.
Linseed (2 samples)	0·8-2·9	
Maize	2·53	
Cotton seed (4 samples of different age)	0·1-6·28	
,,	0·99	1·0
,,	2·0	2·1
,,	0·1	
Rape	2·15	
Croton (2 samples)	21·08	
Castor (3 samples)	0·0	
Olive	2·54	
Japan fish	1·78	
Fish, containing coast cod oil, etc.	9·22	
Cod liver, kept some years in bottle	2·60	
,, fresh	3·60	
Skate liver	0·80	
Shark liver	2·95	
Seal	1·50	
Horses' foot	4·07	
"Animal" oil	3·73	
Palm, containing 23·8 per cent free fatty acids	2·34	
Sawarri	1·07	
Cacao butter	2·80	
Palm nut, containing 6·68 per cent free fatty acids	19·55	
,, ,, 6·94 ,, ,, ,,	11·4	
,,	11·6	
,,	22·2	
,,	19·89	20·38
Cocoa nut, containing 9·9 per cent free fatty acids	12·71 12·29	
,, ,, 3·9 ,, ,, ,,	20·9	
,,	21·9	
,,	26·7	
,,	26·59	
,, containing 13·25 per cent free fatty acids	26·4	
,,	28·2	30·0
,,	30·4	
Japan wax (2 samples)	5·6-10·05	
Lard	6·6	
Beef marrow	2·40	
Bone fat, containing 42·6 per cent free fatty acids	4·22	
Tallow, South American	7·24	
,, home melt I.	1·3	
,, ,, II.	4·8	6·0
,, ,, III.	1·4	1·7
,, premier jus	0·58	
Butter fat I.	49·3	
,, containing 0·56 per cent free fatty acids II.	43·32	
,,	41·4	
,,	32·0	31·3
,, containing margarine, free from cocoa nut oil	12·8	

Irregularities in the results due to variations in the time allowed for distillation, the varying level of the liquid, etc., are said to be avoided by employing a special contrivance designed by *Amberger*.[1]

It will be seen from the table that in the case of those oils which in their fresh state have a very low *Reichert* value, the amount of volatile acids increases with age. This is especially exemplified by cotton seed oil and tallow.

The absolute quantity of the volatile fatty acids can be found approximately by evaporating down the neutralised solution containing the potash salts of the volatile fatty acids to a small bulk, and finally drying in an oven to constant weight.[2] By deducting from the weight thus found the weight of K_2O calculated from the amount of potassium hydrate used for the neutralisation of the volatile fatty acids, the amount of anhydrides of the volatile fatty acids is obtained. From this the mean molecular weight of the volatile fatty acids can be calculated (cp. Vol. II. Chap. XIV. "Butter Fat"). It should, however, be noted that this method does not yield strictly accurate results as the method is not free from errors (cp. also footnote 4, p. 525).

The volatile acids to be considered here are the following: butyric, caproic, caprylic, capric, and also lauric. *Butyric* acid is completely soluble in water, whereas *lauric* acid is only slightly soluble in large quantities of boiling water. *Capric* acid is almost insoluble in cold water. *Caproic* and *caprylic* acids occupy an intermediate position. 100 c.c. of water at 15° C. dissolve of caproic acid 0·882 grms., and of caprylic acid 0·079 grms. The solubilities vary considerably, however, in the case of mixtures of these two acids. The solubilities of caproic and caprylic acids in water increase so considerably with the rise of temperature, that they can be dissolved completely by large quantities of boiling water. Hence the *volatile* acids have been considered by some chemists as being practically identical with the *soluble* acids.

The demarcation between *volatile* and *non-volatile* acids is not an absolute one, and much depends on the conditions under which the distillation is carried out; for small quantities of insoluble acids, notably myristic and palmitic acids, and even stearic acid, are carried over in the distillation processes of *Polenske* and of *Müntz and Coudon* (see Chap. VI.) if only small quantities of fatty material are worked upon. Thus *Arnold*[3] obtained in the case of tallow and lard small amounts of a "volatile" acid which was found on further examination to be nothing else than palmitic acid (see Vol. II. Chap. XIV. "Lard," "Tallow").

The several *volatile fatty acids* differ in their solubility in *water*. An approximate separation of the volatile fatty acids into

(1) Soluble volatile acids,
(2) Insoluble volatile acids

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909, xvii. 26.

[2] Cp. Fendler and Frank, *Zeits. f. angew. Chem.*, 1909, 256.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 151.

is attempted in the conventional *Reichert* process. As indicated on p. 417, the 110 c.c. of distillate obtained in that process are filtered; thus the insoluble volatile acids, which have been carried over to some extent by the water vapours, are separated from the soluble volatile acids. The notes given on p. 418 show, however, that even the most readily soluble acid, viz. butyric acid, is not driven off completely, whereas the much less soluble caproic acid is obtained almost completely in the filtered distillate. It must, therefore, be understood that varying quantities of the several "soluble" acids in the distillate have a considerable influence on the relative solubility of each individual fatty acid. To illustrate this by a further example: In the case of cocoa nut oil, which contains no butyric acid, the 110 c.c. of distillate as obtained by *Reichert's* process are completely saturated; this is indicated by the milky turbidity which the filtered distillate exhibits.

In order to show the rate at which butyric, caproic, and caprylic acids are volatilised from their aqueous solutions the following table, due to *Duclaux*, may be given. The percentage numbers were obtained in ten successive fractions of 10 c.c. each, when 100 c.c. were distilled off from 110 c.c. of the saturated solutions of the several fatty acids.

Fraction.	Butyric Acid.	Caproic Acid.	Caprylic Acid.
	Per cent.	Per cent.	Per cent.
1	17·1	33·5	55·5
2	32·7	56·0	78·0
3	46·5	75·5	91·0
4	58·5	86·0	93·0
5	68·8	92·5	95·0
6	77·5	96·5	96·8
7	84·3	97·5	97·8
8	90·2	98·4	99·0
9	94·6	99·3	99·5
10	97·5	100·0	100·0

Soluble Volatile Acids

In the absence of satisfactory methods for the determination of the *soluble volatile acids* a number of conventional methods, simulating in their importance the "quantitative reactions," have been suggested, especially with a view to the examination of butter fat. The following methods are examples of this kind. If carried out under strictly identical conditions, they furnish comparable results. It should, however, be distinctly understood that the "soluble acids" found by the following processes are not identical with "volatile acids," and that at best the tests described furnish only a measure of the dissolved acids, *i.e.* of the acids dissolved under the prescribed conditions.

(1) Saponify[1] 4 to 5 grms. of an oil or fat as described Chap. VI. p. 379; thus the saponification value of the sample is found. The alcohol is then evaporated off, the soap is dissolved in water, and

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[1] Cp. Bondzyński and Rufi, *Journ. Soc. Chem. Ind.*, 1890, 44

decomposed with hydrochloric acid. The liberated fatty acids are washed on a filter with hot water, as described under "Insoluble Fatty Acids." The insoluble fatty acids are then dissolved in neutralised alcohol, and their neutralisation value is determined by titration with half-normal caustic potash. By subtracting this neutralisation value from the saponification value, the amount of potassium hydrate required for the neutralisation of the dissolved ("soluble," "volatile") fatty acids is obtained.

Example.—For the saponification of 5 grms. of a butter fat 1130 mgrms. of potassium hydrate (KOH) were used, and for the neutralisation of the insoluble fatty acids 920 mgrms. were required. The difference $1130 - 920 = 210$ corresponds to the alkali required for the soluble fatty acids in 5 grms. of butter fat. Hence, 42 mgrms. of potassium hydrate (KOH) have been used per grm. of butter fat.

If the mean molecular weight of the dissolved fatty acids be known, their absolute quantity can be calculated (cp. Chap. XI. p. 639).

(2) Another method is based on the fact that the ratio between the quantities of alkali requisite for the neutralisation of the dissolved fatty acids on the one hand, and of the insoluble fatty acids on the other, is constant for any given fat (*Morse and Burton* [1]).

These relative quantities are given in the following table :—

Kind of Fat.	Per cent KOH required for	
	Insoluble Acids.	Dissolved Acids.
Butter fat	86·57	13·17
Cocoa nut oil, not washed	91·85	8·17
,, ,, washed with hot water . . .	92·43	7·42
,, ,, ,, ,, dilute soda . .	92·33	7·45
Cotton seed oil	92·05	7·76
Lard	95·96	3·82
Beef tallow	96·72	3·40
Oleomargarine	95·40	4·57

The following four standard solutions are required :—

1. Hydrochloric acid, 1 c.c. of which is equivalent to 20 mgrms. KOH.
2. Hydrochloric acid, 1 c.c. of which is equivalent to 2 mgrms. KOH.
3. Alcoholic potash (prepared with 95 per cent alcohol) approximately corresponding to acid No. 1. The strength of the potash solution must be determined accurately by titrating with the acid.
4. Alcoholic potash, corresponding to acid No. 2.

The analysis is carried out as follows :—

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[1] *Journ. Soc. Chem. Ind.*, 1888, 697.

Place from 1 to 2 grms. of the dried and filtered fat—the exact quantity need not be ascertained—in an *Erlenmeyer* flask of 250 c.c. capacity, and saponify with that amount of the strong potash solution which exactly equals 40 c.c. of the strong standard hydrochloric acid. Then add phenolphthalein, and titrate back the excess of alkali with the standard hydrochloric acid. (Thus the *saponification value* may be found.) Evaporate off the alcohol on the water-bath, and exactly liberate the fatty acids by adding just enough of the weaker standard acid; this quantity is, of course, the difference between 40 c.c. and the number of c.c. used for neutralising the excess of alkali after saponification. Next fit the flask with a condensing arrangement, consisting of a glass tube about 400 mm. long and 5 mm. in diameter, having its upper end bent downwards, and attached to a small U-tube containing water. This is designed to prevent the escape of volatile acids during the heating, which is continued until the contents of the flask become clear. Then filter the solution, to which the liquid from the U-tube is added, through thick, well-wetted paper, and wash the insoluble fatty acids until the filtrate measures 1000 c.c. Next dissolve the insoluble acids in 50 per cent alcohol, and titrate with the strong potash solution; finally titrate the soluble acids with the weak potash solution.

The ratio only between the two amounts of alkali being required, it is neither necessary to weigh the fat nor to know the absolute strength of the standard alkalis.

(3) The French official method for the determination of "volatile fatty acids" in butter fat as prescribed by an Act of April 16, 1897, is based on earlier proposals by *Dupré*,[1] and is fashioned after the *Reichert-Wollny* process. In this method 5 grms. of (butter) fat are saponified, and 400 c.c. of distillate are collected, the condensed distillate, as it comes over, being passed through a small filter, on which the insoluble volatile acids are collected. The 400 c.c. of filtered distillate are then titrated with a standard alkaline solution, and the number of c.c. used is *calculated to butyric acid.*

For the details of the method, which must be rigorously adhered to in order to obtain comparable results, the reader is referred to the French edition of this work.[2]

Insoluble Volatile Acids

The determination of the insoluble volatile fatty acids (left on the filter in the *Reichert* process and in the French official method), by weighing the residue left on the filter, must be out of the question, as the loss incurred on drying the acids is too great. This is exemplified by the numbers (ascertained in the author's laboratory and) given in the following table :—

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[1] *Analyst*, 1877, 87.

[2] Lewkowitsch, *Technologie et Analyse chimiques des Huiles, Graisses et Cires*, Paris, 1906, pp. 460-463. Cp. also Müntz and Coudon's Method, Vol. II. Chap. XIV. "Butter Fat."

Loss of Volatile Acids on drying on the Water-bath (*Lewkowitsch*)

	After ½ hour.	1 hour.	1½ hours.	2 hours.	2½ hours.
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Butyric . . .	16·88	28·96	31·20	45·13	...
Caproic . . .	2·18	3·88	4·54	9·06	10·47
Caprylic . . .	0·82	1·24	1·52	2·41	3·17
Capric . . .	0·12	0·22	0·29	0·39	0·51
Lauric . . .	0·25	0·26	0·29	...	...

The same difficulty which attaches to the complete determination of the soluble volatile fatty acids is also met with in the determination of the insoluble volatile fatty acids. The difficulty has been overcome by adopting the expedient employed in the *Reichert* process, *i.e.* by titrating a definite amount of insoluble volatile acids. This is done by the processes recommended respectively by *Polenske* and *Müntz and Coudon* (see Chap. VI. p. 425).

It has been shown above, p. 427, why it is imperative to adhere to the prescribed quantities. The above given tables may be supplemented by the following table reproducing a selection from experiments made by *Heiduschka and Pfizenmeier*[1] with *pure* fatty acids. The influence of the quantity of substance taken is clearly brought out.

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[1] *Beiträge zur Chemie und Analyse der Fette*, München, 1910, pp. 14, 23.

[Table

	$\frac{1}{10}$ c.c. KOH for Soluble Volatile Acids by *Reichert's* Process.						$\frac{1}{10}$ c.c. KOH for Insoluble Volatile Acids by *Polenske's* Process.					
	Substance taken.	Per cent of Theory.	Substance taken.	Per cent of Theory.	Substance taken.	Per cent of Theory.	Substance taken.	Per cent of Theory.	Substance taken.	Per cent of Theory.	Substance taken.	Per cent of Theory.
	0·5 grm.		1·0 grm.		3·0 grm.		0·5 grm.		1·0 grm.		3·0 grm.	
Acetic	49·80	59·8	99·91	59·9	. .	. .	(0·20)	(0·24)	(0·20)	(0·12)	. .	. .
Butyric	52·81	93·0	105·26	92·6	. .	. .	(0·20)	(0·36)	(0·26)	(0·23)[1]	. .	. .
Caproic	39·66	92·0	65·89	76·4	93·50	36·2	0·40	0·93	9·10	10·56	117.00	45·00
Caprylic	12·30	35·7	12·34	17·8	15·98	7·7	21·00	60·76	49·35	71·00	144·30	69·31
Capric	1·52	5·2	1·69	2·9	1·70	0·4	27·60	95·03	34·00	58·50	43·90	25·19
Lauric	0·66	2·6	0·72	1·4	0·83	0·6	7·80	31·20	8·50	17·00	8·80	5·90
Myristic	0·62	2·8	0·70	1·6	1·02	0·8	2·00	9·10	2·30	5·27	2·40	1·80
Palmitic	0·60	3·0	0·65	1·7	1·05	0·9	0·90	4·60	0·90	2·30	1·00	0·85
Stearic	0·50	2·8	0·46	1·3	0·53	0·5	0·65	3·70	0·70	2·00	0·62	0·59
Oleic	0·66	3·6	0·71	2·0	0·95	0·9	0·68	3·86	0·70	2·00	0·70	0·65
Linolic	0·63	3·5	0·65	1·8	0·81	0·7	0·41	2·28	0·40	1·12	0·50	0·47

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[1] These numbers are of course only due to the errors of the method and are to be taken as tantamount to nil.

With 5 grms. of caprylic acid and the usual amount of water and glycerin and dilute sulphuric acid as if the triglyceride had been used, the sum of the *Reichert-Meissl* value and the titration number of the insoluble volatile fatty acids was 171·3. This shows that the total amount of the fatty acids distilled over was only 49·3 per cent of the quantity taken. With 7 grms., the total sum of the *Reichert-Meissl* value and the titration number for the insoluble volatile fatty acids was 171·8; this shows that only 35·35 per cent of the total amount taken had distilled over.

These methods require the strict observance of the most minute details. As they have been specially adapted to the examination of butter fat, the details will be given under the heading of "Butter Fat" (Vol. II. Chap. XIV.), where further references to the method will be found with a view to detecting the presence of cocoa nut oil.

The differentiation of the insoluble volatile acids from the soluble volatile acids and the accurate determination of both is of the greatest importance in the examination of butter fat and the detection of cocoa nut oil and (or) palm nut oil therein, and in other edible fats generally.

Stress has been laid on the fact that, notwithstanding their excellence the *Reichert* and *Polenske* processes only afford limited information, and in certain cases fail to supply the desired answer. This is to some extent due to the feature that only part of the acids is recovered, and that even that part cannot be determined quantitatively with greater accuracy than is warranted by the approximate method described, p. 417. Nevertheless, these processes enable us to establish chemically the difference between butter fat on the one hand, and cocoa nut and palm nut oil on the other with ease, and to ascertain the respective mean molecular weights of the volatile soluble and of the volatile insoluble fatty acids of these two kinds with sufficient accuracy for technical purposes. It is only when mixtures of these two kinds of fats are under examination that difficulties arise. More difficult still becomes the analytical problem when these two kinds of fats are admixed with such fats as lard, tallow, cotton seed stearine—a problem which presents itself frequently in the examination of margarines and mixed edible fats.

Hence endeavours are continuously made to extend and invent new methods of research. The investigation of the metallic salts of the volatile fatty acids—silver salts, barium salts, zinc salts, cadmium salts—on the one hand, and of the ethyl esters on the other have been undertaken, but hitherto no such practical method has been evolved as can be placed before the reader in this chapter. These methods will be considered in some detail in Chapter XII. In the following volumes it will be shown under the headings "Lard," "Butter Fat," "Margarine," how far the problem can be solved with the aid of the methods described in this and the foregoing chapters.

5. Separation of Insoluble Saturated from Unsaturated Fatty Acids

The presence of unsaturated fatty acids in the mixed insoluble fatty acids is detected in the readiest manner by determining the iodine value of the mixed fatty acids; this method offers an additional advantage in that it furnishes a measure of the unsaturated fatty acids, much as the iodine value of the oils and fats affords a measure of the unsaturated glycerides.

If no definite iodine absorption be found, it is safe to conclude that unsaturated fatty acids are absent.

The mixed fatty acids as obtained from the natural oils, fats, and waxes always have a definite iodine value. From it some preliminary information may be obtained by reference to the following table:—

Iodine Values of the Insoluble Fatty Acids

Oils and Fats

Oil.	Class of Oil.	Group.	Iodine Value.
Perilla	Drying oils		210·6
Linseed			179-209·8
Tung {Chinese Japanese}			144-159
Lallemantia			166
Candle nut			142·7-144·1
Stillingia			161·9-181·8
White acacia			160·7
Cedar nut			161·3
Garden rocket			157
Hemp seed			141
Buckthorn			160·6
Burdock			162
Gynocardia			162·6
Walnut			150
Linaria			148·5
Safflower			132·5-148·2
Kaya			149·5
Echinops			139·1-143·8
Soya bean			138-142
Poppy seed			139
Manihot			143·1
Millet seed			134·3
Sunflower			124-134
Yellow acacia			131·7
Para rubber tree seed			127·3
Service berry			127·5
Fir seed			121·5
Madia			120·7
Strawberry seed			191-193
Raspberry seed			181·3
Hawthorn seed			174·3
Currant seed			159·5
Blackberry seed			155·1
Cameline	Semi-drying oils	Cotton seed oil group	136·8
Grape seed			99-135
Celandine			127·3
Clover, red			126·2
,, white			122·2
Water melon			122·7
Maize (corn)			119·5
Wheat			123·3
Beech nut			114
Kapok			108
Cotton seed			111-115
Sesamé			110·45
Croton			111·5
Curcas (purging nut)			105·1
Brazil nut			108
Tomato seed			129·6
Mucuna			112·9
Sorghum			101·63

Iodine Values of the Insoluble Fatty Acids—continued

Oils and Fats—continued

Oil.	Class of Oil.	Group.	Iodine Value.
Spindle tree			105·3
Garden cress		Rape oil group	111·4
Ravison			126·1
Rape (colza)			99-103
Black mustard			109·6
White mustard			95·3
Radish seed			97·1
Jamba			96·1
Quince	Non-drying oils		124·6
Cherry kernel			109
Cherry laurel			112·1
Apricot kernel			103
Plum kernel			103 (?)
Peach kernel			94-101
Almond			93-96·5
Sanguinella			102·8
Arachis			96-103
Rice			97·4-109
Tea seed			90·8
Tsubaki			83·7
Sasanqua			86·1
Pistachio			88·9-96·2
Hazel nut			87·5-90·3
Elderberry			93
Olive			86-90
Calophyllum			92·2
Coffee berry			89·5
Ungnadia			86·5
Paradise nut			72·3
Secale			75·8
Canari			67·2
Castor		Castor oil group	87·93
Cod liver	Marine animal oils	Liver oils	130·5-170
Seal		Blubber oils	186·5-201
Whale			131·2
Turtle			119
Brown fish			126
Chrysalis	Terrestrial animal oils		135·8
Egg			72·9
Neat's foot			61·9-75·8

Iodine Values of the Insoluble Fatty Acids—continued

Oils and Fats—continued

Oil or Fat.	Class of Fat.	Group.	Iodine Value.
Chaulmoogra . .	Vegetable fats	Chaulmoogra oil group	86-103
Hydnocarpus . .			106·3
Lukrabo . . .			87·8
Laurel . . .		Laurel oil group	81·8
Mowrah seed . .			56·6
Palm . . .		Palm oil group	53·3
Gamboge butter .			56·4-57·8
Akee . . .			58·4
Macassar . . .			50·2
Sawarri . . .			51·5
Mafura tallow . .			47·5
Nutmeg butter .		Myristica group	31-6
Ochoco . . .			1·47
Mkányi . . .		Cacao butter group	42·1
Shea butter . .			55·6-57·2
Rambutan tallow .			41·0
Cacao butter . .			33-39
Chinese vegetable tallow . . .			30·55
Borneo tallow . .			31·5
Maripa . . .		Cocoa nut oil group	17
Palm nut . .			12·0
Cocoa nut . .			8·4-9·3
Kusu . . .		Dika fat group	5·1
Blackcock . .	Animal fats	Semi-drying fats	120
Lynx . . .			111·8
Marmot . . .			105·6
Horse . .			84-87
Hare . . .			93·3
Rabbit (wild) . .			101·1
Rabbit (tame) . .		Non-drying fats	64·4
Horse marrow . .			71·8-72·2
Goose (domestic) .			65·3
Goose (wild) . .			65·1
Chicken . . .			64·6
Polecat . . .			60·6
Human, adult . .			64
Lard . . .			64
Fat from wild boar .			81·2

Iodine Values of the Insoluble Fatty Acids—continued

Oils and Fats—continued

Oil.	Class of Fat.	Group.	Iodine Value.
Dog	Animal fats.		50·15
Wild cat			58·8
Domestic cat			54·8
Beef marrow			55·5
Bone			55·7-57·4
Beef tallow			41·3
Mutton tallow			34·8
Elk			31·9
Roebuck			28·9
Fallow buck			28·2
Stag			23·6
Butter		Milk fats	28-33
Sperm oil	Liquid waxes		83·2-85·6
Arctic sperm oil			82·7
Wool wax	Solid waxes	Animal waxes	17

The above iodine values refer to the mixed *insoluble* fatty acids as prepared by the method described in Chapter III. p. 109. Hence the numbers given in the foregoing table do not necessarily stand in strict correspondence with the iodine values of the natural oils, fats, and waxes from which they have been derived; for the influence, which soluble fatty acids, as also mono- and di-glycerides in the original substances, exercise severally on the iodine values of the glycerides, disappears in the case of the mixed fatty acids.

This will be seen at a glance on referring to the table given Chap. VI. p. 406, and comparing the iodine values of mono-, di-, and triglycerides with the corresponding iodine values of their fatty acids. It follows that it is not always permissible to calculate the iodine value of an oil or fat from the iodine value of its insoluble fatty acids; in the case of waxes this is still less permissible.

If only one unsaturated acid be admixed with the saturated acids, and the chemical composition of the unsaturated fatty acid be known, it is possible to calculate its absolute quantity from the iodine value, with the assistance of the table given Chap. VI. p. 406. Thus if a given mixture of fatty acids have the iodine value 45·035, and it be known that the mixed fatty acids consist of saturated fatty acids and oleic acid only, then the absolute quantity of oleic acid will be found from the following proportion :—

$$90{\cdot}07 : 100 : : 45{\cdot}035 : x\,;\ x = 50 \text{ per cent.}$$

Even if a mixture of two unsaturated fatty acids of known composition, *e.g.* oleic acid and linolic acid, be present, the respective amounts of oleic and linolic acids can be calculated from the iodine value of the mixed fatty acids, if the absolute quantity of the solid acids (and hence also of the unsaturated acids) be known.

Such information would be furnished by a method permitting the quantitative separation of the saturated from the unsaturated acids. The several methods proposed hitherto for this purpose will be described under (*a*), (*b*), and (*c*).

(*a*) *Separation based on the Different Solubility of Salts of Fatty Acids in Organic Solvents*

An analytical process for the separation of solid fatty acids from liquid acids was first proposed by *Gusserow*;[1] *Varrentrapp*[2] was the first to employ this method for the separation of oleic acid. It is based on the solubility of the lead salts of the liquid fatty acids (oleic, linolic, linolenic, etc.) in ether, in which the lead salts of the higher solid fatty acids, *e.g.* stearic and palmitic, are practically insoluble, as will be gathered from the following table :—

Lead Salt of	100 c.c. of Ether dissolve	Observer.
	Grms.	
Palmitic acid . . .	0·0184	Lidoff[3]
Stearic acid . . .	0·0148	,,
Mixed stearic and palmitic acids (iodine value = 0)	0·0150 (at 25° C.)	Twitchell[4]

In former editions the author had pointed out that many observations made in his laboratory led him to the conclusion that lead myristate, lead laurate, and the lead salts of still lower saturated fatty acids were very appreciably soluble in ether. On the author's suggestion *Neave* made a study of the solubilities of the lead salts of caproic, caprylic, capric, lauric, and myristic acids, the results of which are given in the table Chap. III. p. 142. There are also added therein the solubilities of the lead salts of palmitic, stearic, and oleic acids.

It should be noted that the solubilities in ether of the lead salts of the solid saturated fatty acids are much increased if the ether holds in solution notable quantities of lead salts of oleic and less saturated acids. Hence the *Gusserow-Varrentrapp* process does not yield strictly accurate results, inasmuch as small quantities of the lead salts of saturated solid acids pass into the ethereal solution (as was shown first by *Mulder*[1]), whilst lead salts of unsaturated fatty acids remain partly undissolved. *Lewkowitsch*[2] also has shown that a complete separation of the liquid from the solid acids cannot be thus effected. Therefore, the separation by means of the lead salts should be looked upon as a partial separation only.

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[1] *Liebig's Annal.*, 1828 (27), 153.

[2] *Ibid.*, 1840 (35), 197.

[3] *Berichte*, 1893 (26), Ref. p. 97.

[4] *Journ. Soc. Chem. Ind.*, 1895, 515.

The lead salts of the saturated as also of the unsaturated fatty acids are more readily soluble in *dry* ether than in moist ether. If the latter is used, a larger amount of lead salts of the unsaturated acids remain undissolved, so that the percentage of solid acids is found too high. Again, on using dry ether, the results are a few per cent too low.[3]

It must further be borne in mind that the *Gusserow-Varrentrapp* method effects chiefly the separation of *insoluble solid* from *insoluble liquid* acids, which is not tantamount to the separation of *saturated* from *unsaturated* fatty acids, since the lead salts of the solid isomerides of oleic acid, viz. elaïdic, "isoöleic," petroselinic, and cheiranthic acids are sparingly soluble in cold ether. This is especially the case with *erucic acid* (see below). This should be remembered as in the literature on this subject unsaturated fatty acids are very frequently considered as coterminous with liquid acids. It may be added that gadoleic acid, melting at 24·5° C., also yields a sparingly soluble lead soap. Gadoleic acid stands midway between oleic and erucic acids as regards the solubility of its lead salts in ether.

The solubilities of the lead salts of fatty acids would thus point to the possibility of subdividing the latter into three groups:—

(1) Fatty acids, the lead salts of which are practically insoluble in ether: palmitic, stearic, arachidic, behenic.

(2) Fatty acids, the lead salts of which are sparingly soluble in cold ether: erucic, petroselinic, "isoöleic."

(3) Fatty acids, the lead salts of which are easily soluble in ether, especially in warm ether: oleic, linolic, linolenic, clupanodonic.

It is obvious that a quantitative separation of the three groups cannot be effected, if a mixture of the several fatty acids be present, not only because the line of demarcation covers too great a range of temperature, but especially because the solubilities of the lead salts of fatty acids which in their pure state are definite, are entirely different ones[4] in the presence of lead salts of unsaturated fatty acids, as pointed out above. In a large number of experiments made by the author on the lines suggested by the subdivision pointed out above (although quantitative results could not be expected), it was possible to resolve complicated mixtures of fatty acids approximately into three groups, a further examination of which, by applying other methods, enabled the author to gain a more complete insight into the composition of such mixtures than was hitherto possible by the mere separation of the lead salts by hot ether.

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[1] Mulder, *Chemie der austrocknenden Oele*, 1867, p. 44 (German translation).

[2] *Journ. Soc. Chem. Ind.*, 1890, 845. Cp. Vol. II. Chap. XIV. "Linseed Oil."

[3] Fahrion, *Zeits. f. angew. Chem.*, 1904, 1488. A table is given there showing that on treating tallow by the lead-salt-ether-method under varying conditions, solid acids were obtained, the iodine values of which varied from 4·3 to 12·1.

[4] Thus if only a few per cent of solid acids be present no lead salts will separate from the ethereal solution.

Notwithstanding its drawbacks and restrictions in its application, the *Gusserow-Varrentrapp* method is at present the best at our disposal and may be considered a method of separating "solid" from "liquid" acids. This method has been modified by several observers. I omit the description of those modifications which yield somewhat erratic results or have proved inconvenient in practical work, such as *Oudemans'*,[1] *Kremel's*,[2] and *Röse's*[3] proposed modifications. The reader must therefore be referred to the original papers (or to the second edition of this work, pp. 193 and 194). I describe somewhat fully a combination of *Muter and de Koningh's*[4] modification with *Lane's*[5] suggestion, amplified by such explanatory details in working the method as have been found useful in my laboratory.

For the separation of "solid" acids from "liquid" acids, either the mixed fatty acids or their glycerides may be employed. In the latter case three to four grms. of the sample are saponified in the usual manner with 50 c.c. of approximately half-normal alcoholic[6] potash in a 300 c.c. flask. Phenolphthalein is added, the solution is slightly acidified with acetic acid, and finally titrated with alcoholic potash until neutral. The bulk of the alcohol is best driven off by distillation. When starting with mixed fatty acids, they are neutralised with aqueous half-normal potash. The solution is then diluted with water to about 100 c.c. Next 30 c.c. of a 10 per cent lead acetate solution are diluted with 150 c.c. of water, brought to the boiling point, and gradually run into the soap solution with constant shaking, so that the separating lead soap is made to adhere to the side of the flask, when the solution cools. The flask containing the lead soap is filled completely with hot water, and then allowed to cool. When the liquid has become clear, it is poured off through a filter. As a rule, the solution is so clear that no solid particles will be found on the filter; should there be any, they must be brought back into the flask. The precipitate in the flask is washed thoroughly with boiling water, using the precaution to cool the hot solutions before filtering, thus causing the lead salts to adhere to the sides of the flask. The last drops of water may be removed by means of a thin roll of filter paper. It is not advisable to dry the lead salts, as in the case of drying oils they absorb oxygen from the air somewhat rapidly. Next 150 c.c. of ether are added to the lead salts, and the flask is corked and shaken repeatedly, so that the lead salts may disintegrate. The flask is then attached to a reflux condenser and heated on a water-bath for some little time with frequent shaking.

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[1] *Journ. f. prakt. Chem.* 99, 407.

[2] *Pharm. Centralh.* 5, 337.

[3] *Journ. Soc. Chem. Ind.*, 1887, 306.

[4] *Analyst*, 1889, 61.

[5] *Journ. Amer. Chem. Soc.*, February 1893.

[6] The alcohol should be pure, for impure alcohol is likely to lead to low iodine values of the unsaturated fatty acids (Wesson and Lane, *Journ. Soc. Chem. Ind.*, 1905, 714).

The lead salts of the liquid fatty acids dissolve readily in the hot ether, conjointly with some portions of the salts of the saturated acids. When the undissolved salts (if any) settle out at the bottom of the flask as a fine powder, the heating is interrupted. If all operations are conducted somewhat rapidly, and unnecessary exposure to the air is avoided, working in an atmosphere of an inert gas can be dispensed with. The ethereal solution is then allowed to cool down to the ordinary temperature and filtered through a plaited filter, kept covered with a watch-glass, into a separating funnel. The insoluble salts are brought on to the filter by washing the flask three or four times with ether, using 30 c.c. each time. The ethereal solution is then shaken with a mixture of one part of hydrochloric acid and four parts of water, in order to decompose the lead salts. The ether dissolves the free fatty acids as they are liberated, whilst the undissolved lead chloride settles out at the bottom of the separating funnel. After separating into two layers, the acid liquid is drawn off and the ethereal layer washed with small quantities of water until the wash-water is free from acid. Finally, the ethereal solution is filtered through a small plaited filter [1] into an ordinary flask. In case the liquid fatty acids consist chiefly of oleic acid, the result will be sufficiently accurate if the ether is evaporated off on the water-bath and the residue dried in a water oven. If, however, the presence of less saturated fatty acids (as in linseed, soya bean, maize, and marine animal oils) than oleic is suspected, the ethereal solution should be distilled off in a current of dry hydrogen or dry carbon dioxide. The flask is then immersed up to the neck in warm water, which is finally brought to the boiling point. Thus the last traces of moisture are removed.

This *modus operandi* has been found preferable to the use of a *Muter* tube (which involves making up the ethereal solution of the liquid fatty acids to 250 c.c., and determining the acids in an aliquot portion), as the drawing off of the ethereal solution is very apt to lead to errors. If it be desired, in special cases, *e.g.* for the subsequent determination of the iodine value of the liquid fatty acids, to avoid exposure to the atmosphere during the weighing out of a portion of the liquid acids, the ethereal solution of the liquid fatty acids may be made up to a volume of 200 or 250 c.c. 50 c.c. are then taken out by means of a pipette and transferred to a stoppered bottle; the ether is evaporated off in a current of hydrogen or carbon dioxide. Then a standardised iodine solution is introduced and the iodine absorption determined in the usual manner. In this case the weight of substance taken is best determined in *another* portion of 50 c.c.,[2] which is treated in the manner described above. It will thus be seen that at the same time the iodine value of the liquid fatty acids can be ascertained. In fact this should be always done, since very valuable information as to the nature of the liquid fatty acids is derived from their iodine values. In the case of drying oils it is imperative to drive off the ether in a current of hydrogen or carbon dioxide, as will be gathered from the following numbers obtained in my laboratory by *J. H. Walker*:—

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[1] Wesson and Lane (*Journ. Soc. Chem. Ind.*, 1905, 715) recommend to use a Büchner filter.

[2] Cp. v. Raumer, *Zeits. f. angew. Chemie*, 1897, 210; 247.

Oil.	Iodine Value of the Liquid Fatty Acids.	
	Ether distilled off without using an Indifferent Gas.	Ether distilled off in a current of Carbon Dioxide.
Linseed	204·7	209·8
Candle nut . . .	183·0	185·7

It is advisable to isolate the "solid" fatty acids from the lead salts, and determine their weight. This will provide a check for the accuracy of the analysis, as the sum of the "solid" and "liquid" acids should furnish approximately the weight of the original fatty acids. Furthermore, the iodine value of the "solid" acids will indicate how much of the liquid acids has remained undissolved. The acids may then be further examined by ascertaining their melting point, mean molecular weight, etc.

It must be pointed out that the isolation of the "solid" fatty acids from their lead salts is not an easy operation with acids of high melting points (palmitic, stearic, arachidic, behenic, etc.), as the solid fatty acids readily occlude undecomposed lead salt, so that the mineral acid cannot readily attack them. Hence frequent boiling up is required, to remove the last traces of metal. The acids should not be considered free from metal, unless examination has shown them to yield no ash on incineration.

In order to show that only an approximate separation is effected by this method, I give in the following table some results obtained in my laboratory by *H. E. Clapham*:—

Substance.	Weight used. G.	Ether Volume.	Temperature at which Ether Solution was kept.	Liquid Fatty Acids. Per cent.	Solid Fatty Acids. Per cent.	Iodine Value of Acids.		Loss. Per cent.
						Liquid.	Solid.	
Cocoa nut oleine	3·3821	200 c.c.	15°-18° C.	24·36[1]	...	37·35	...	...
	3·3931	200 c.c.	15°-18° C.	24·76	...	35·40	...	...
Whale oil	3·2791	75 c.c.	44° F.=6·7° C.	77·28	19·78	126·86[2]	21·35	2·94
,, ,,	3·3124	75 c.c.	44° F.=6·7° C.	78·76	17·93	126·08	19·77	3·31

The accuracy of the results depends on the temperature to which the ethereal solution is cooled and also on the quantity of ether used;

[1] If the soluble acids have not been removed by washing, they will be found to the largest extent in the ethereal solution.

[2] For the true iodine value cp. p. 562.

by varying these two factors different results are obtained. Losses amounting to several per cent are not easily avoidable. From the second series of experiments the conclusion must be drawn that too little ether was used, but even on employing larger quantities it is not possible to free the " solid " acids completely from the unsaturated acids (cp. Vol. II. Chap. XIV. " Linseed Oil ").

If larger quantities of ether be used, more of the lead salts of saturated acids pass into the ethereal solution.

In place of ether, other solvents, such as petroleum ether boiling below 80° C. (*Twitchell* [1]), and benzene (*Farnsteiner* [2]), have been proposed. An important observation with regard to petroleum ether was made by *Lane*,[3] who found that lead ricinoleate is insoluble in low boiling petroleum ether. It is therefore possible to separate ricinoleic acid from other unsaturated fatty acids (cp. below, p. 580). The solubilities of the lead salts of some fatty acids are given in *Neave's* table reproduced Chap. III. p. 142.

Farnsteiner's method is based on the solubility, at the ordinary temperature, of the lead salts of " liquid " fatty acids in *benzene*, wherein the lead salts of " solid " fatty acids are practically insoluble at temperatures below 8° or 12° C. At a somewhat elevated temperature even these salts dissolve in benzene, but on cooling to 8° or 12° C. they separate out in a crystalline form admitting of their being readily filtered off. Thus it was found that 100 c.c. of benzene dissolved only 0·0032 grm. of the lead salts of the solid tallow fatty acids. The solid acids, prepared by repeated crystallisation of the mixed fatty acids from alcohol, melted at 62°-64° C.

The lead salts are prepared as described above, and then dissolved in warm benzene, using 50 c.c. of the solvent for about 1 grm. of oil. On cooling to the ordinary temperature a crystalline deposit separates; the solution is then kept for two hours at a temperature from 8°-12° C. The supernatant liquid is best syphoned off by means of a small thistle funnel, covered with a piece of fine calico (to retain the crystals), and bent twice at right angles so that it may be fitted into a suction bottle connected with a filter pump. (This is preferable to *Farnsteiner's* proposal to force out the liquid by means of air pressure.) The precipitate is washed with 10 c.c. of benzene at 10° C., and again dissolved in 25 c.c. of warm benzene, cooled as before, and the solution filtered off in the manner described. This operation may be repeated a third time so that there are obtained finally from one grm. of oil about 120-130 c.c. of a solution containing the lead salts of the liquid fatty acids. The free fatty acids are prepared as described above.

If benzene free from thiophene be used, the method would offer an advantage for the determination of the iodine value of the unsaturated fatty acids, in that the solvent need not be driven off. This would render this process more convenient than the one described above, provided the quantitative results were better than, or at least equal to, those detailed above. The author calculated, however, from the data given by *Farnsteiner* that the losses, after applying the proper corrections, amount in some cases to 5·8-9·6 per cent. Hence, in the author's opinion, preference should be given to the *lead-salt-ether method.* Possibly better results would be obtained if test experiments were made with larger quantities than were employed by *Farnsteiner*, who worked with 0·5 to 1·0 grm. of mixed fatty acids.

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[1] *Journ. Soc. Chem. Ind.*, 1895, 515.

[2] *Ibid.*, 1898, 804; *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898, 390.

[3] *Journ. Soc. Chem. Ind.*, 1907, 597.

It should be pointed out, in view of some statements contained in the more recent literature on this subject, that it is impossible to generalise and, as has been done by some authors,[1] draw the conclusion that because in a certain case the benzene method yielded better results than the lead-salt-ether method, the latter should be abandoned in every case. It seems that so much depends on the composition of the fatty acids in the individual oils and fats that each case must be considered on its own merits. It is therefore desirable that in the examination of fatty acids by the foregoing methods both the lead-salt-ether method and the benzene method be examined side by side. Thus statistical data would be gathered which might point to a generalisation, or at least to a rule, defining which groups or classes of oils and fats are more satisfactorily examined by one than by the other method. Possibly also in the case of the benzene method, the fractional separation of the lead salts at different temperatures might lead to an approximate separation such as has been indicated above in setting out the three groups of fatty acids obtained by applying cold and hot ether respectively (see p. 544).

If it be merely required to isolate the "liquid" fatty acids for further examination (such as the determination of their iodine value), the process worked out by *Tortelli and Ruggeri*,[2] combining the advantageous features of the foregoing methods, should be employed. This method has been extensively used in the author's laboratory, and can be recommended as giving reliable results. Unfortunately the process does not lend itself to the quantitative determination of the liquid fatty acids. *Tortelli and Ruggeri* operate as follows:—20 grms. of the sample are saponified with 15 c.c. of an aqueous 50 per cent caustic potash solution and 45 c.c. of 95 per cent alcohol. The excess of caustic potash is neutralised with acetic acid, phenolphthalein being used as an indicator. In a half-litre flask 300 c.c. of 7 per cent lead acetate solution are heated to boiling, and the soap solution is poured into it in a thin stream, with constant agitation. The flask is immersed in cold water and kept therein for about ten minutes, again with constant agitation. When the supernatant liquid has become clear, it is poured off and the lead soap washed three times with 200 c.c. of warm (not boiling) water. The soap is allowed to cool and the drops of adhering water are taken off with filter-paper. 220 c.c. of ether are then poured into the flask, the mass is thoroughly agitated, and warmed in a water-bath for twenty minutes until the ether just begins to simmer; the flask is shaken continuously in order to detach all soap from the sides and bottom. The flask is then immersed in cold water of 8°-10° C., and kept therein for *two hours.* The liquid is next filtered through a plaited filter into a 200 c.c. flask having a narrow neck. This flask is filled completely with ether, then well corked and left immersed in running water for twelve hours. As a rule, some precipitate will settle out. The ethereal solution is then poured through a filter into a separating funnel, and the lead soap decomposed with 150 c.c. of 20 per cent hydrochloric acid. After running off the precipitated lead chloride and the aqueous solution, the ether is again shaken with 100 c.c. of hydrochloric acid. The ethereal solution is then washed with 150 c.c. of water, and finally poured through a plaited filter into a flask of about 300 c.c. capacity. Next the ether is distilled off so far that 40 to 50 c.c. remain in the flask. This solution is poured into another flask of about 100 c.c. capacity, fitted with a good cork, and the flask is immersed almost completely in a water-bath. A current of dry carbon dioxide is then passed through the ethereal solution and the water-bath heated until the ether is driven off.

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[1] Matthes and Serger, *Archiv. d. Pharm.*, 1909 (247), 424; Matthes and Boltze, *ibid.*, 1912 (250), 220.

[2] *L'Orosi*, April 1900.

The iodine numbers of the unsaturated fatty acids so prepared are the highest found hitherto, and for that reason must be accepted as being nearest to the true ones. As has been pointed out already, this method does not admit of the quantitative separation of the saturated from the unsaturated acids. Thus in the preparation of the whale oil liquid fatty acids, the iodine value of which was found to be 144·6, the undissolved lead salts yielded acids having as high an iodine value as 70·0.

A method for the separation of "solid" from "liquid" fatty acids, based on their different solubility in acetone at the freezing point of water and the behaviour of their sodium and potassium salts, does not appear to furnish sufficiently satisfactory quantitative results to be treated here in detail. The reader must, therefore, be referred to the original paper of *Fachini and Dorta.*[1]

(*b*) *Separation by means of Sulphuric Acid and Sulphofatty Acids*

A method of separating saturated from unsaturated fatty acids, based on their behaviour to sulphuric acid, was proposed by *Twitchell.*[2] Whereas the saturated acids are not changed chemically by concentrated sulphuric acid, oleic acid and the less saturated acids combine with concentrated sulphuric acid to form compounds (cp. Chap. III.). Although these are completely insoluble in petroleum ether, whereas the unattacked saturated acids dissolve in this menstruum, a method of separation cannot be based on this difference in solubility, since all fatty acids are more soluble in concentrated sulphuric acid than in petroleum ether. Better results were obtained by *Twitchell* when employing an 85 per cent sulphuric acid, which still forms a chemical compound with oleic acid. The author, however, has shown[1] that this method does not lead to quantitative results; hence it can only be employed for qualitative purposes.

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[1] *Chem. Revue*, 1912, 77.

[2] *Journ. Soc. Chem. Ind.*, 1897, 1002; cp. U.S.A. patent 918,612 (1909).

Lanza (cp. Vol. III. Chap. XV.) found that a dilute solution of stearosulphuric acid is capable of dissolving oleic acid from a mixture of saturated acids and oleic acid, the saturated acids remaining undissolved. *Twitchell*[2] claims the same property for naphthalene stearosulphuric acid (see Chap. II. p. 88, and Vol. III. Chap. XV.). *Lanza's* method of separation is employed on a large scale, but an investigation with a view to using the reaction for analytical purposes has not yet been made.

(c) *Separation by means of the Ammonium Salts*

Falciola[3] bases a method of separating oleic acid from stearic and palmitic acids upon the different solubilities of their ammonium salts in alcohol (Chap. III. p. 140). The mixed fatty acids are dissolved in warm ether, the solution treated with ammonia gas, and then allowed to cool down to the ordinary temperature. The ether is evaporated off, and the residue thoroughly mixed with four times its volume of ammoniacal alcohol, at about 0° C. The precipitate is filtered off with the aid of a pump, and washed with the smallest possible quantity of chilled absolute alcohol. The filtrate and the washings are decomposed with dilute hydrochloric acid, the solvent evaporated off, and the liberated "*liquid*" fatty acids washed, dried, and weighed. The ammonium salts of the "*solid*" fatty acids left on the filter are treated with hydrochloric acid and the separated fatty acids determined in the usual manner. In two test experiments given by *Falciola* in which 60 and 49·6 per cent of oleic acid had been used, there were obtained 63·8 and 49·7 per cent respectively of oleic acid. The recovered "solid" acids amount to 36·20 per cent and 50·3 respectively instead of 40 per cent and 50·4 per cent taken. The total amount of both liquid and solid acids recovered was 102 per cent and 98 per cent respectively.

David[4] also bases a method of separating "solid" from "liquid" acids on the solubility of the ammonium salts of the liquid acids in aqueous ammonia. He claims for this method such an extraordinary accuracy that, on the one hand, 1 per cent of oleic acid may be detected when associated with 99 per cent of solid acids, and on the other hand 1 per cent of a solid fatty acid in admixture with 99 per cent of oleic acid. *David* directs to dissolve 2 grms. of mixed fatty acids in 5 c.c. of warm 95 per cent alcohol, and to add 50 c.c. of ammonia at 22° C. The solution should then be warmed until ammonia escapes.

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[1] Lewkowitsch, *Analyst*, 1900, 64.

[2] *Journ. Amer. Chem. Soc.*, 1906, 196.

[3] *Gazz. Chim. ital.*, 1910 (40), 217.

[4] *Compt. rend.*, 1910 (151), 756.

The solution is allowed to stand at 14° C. (not over 15° C.) and then filtered when the ammonium salts of the solid fatty acids are stated to remain quantitatively on the filter, the ammonium salt of oleic acid passing into the filtrate.

Experiments made in the author's laboratory (by *Stadler*) showed, however, that this method is less accurate than the lead-salt-ether method.

Partheil and Ferié[1] proposed to separate saturated from unsaturated acids *by means of their lithium salts* (cp. table, p. 139). This method was described in the third edition of this work, p. 353, but is omitted here, as *Fahrion*,[2] and also *Farnsteiner*,[3] have shown that the results obtained thereby are untrustworthy.

Methods based on the different solubilities of the unsaturated acids, on the one hand, and the saturated acids on the other, in alcohol and in mixtures of alcohol and benzene (cp. Vol. III. Chap. XV.) have not, up to the present, yielded useful results.

6. Separation and Determination of Individual Solid Fatty Acids—Erucic Acid, Saturated Fatty Acids

The "solid" acids obtained on separating off the "liquid" acids by means of the lead-salt-ether method are but rarely free from unsaturated acids. In the case of rape oil or mixtures containing rape oil, the "solid" acids contain erucic acid (and in the case of marine animal oils, gadoleic acid). A measure of the unsaturated acids can be obtained by ascertaining the iodine absorption of the acids isolated from the insoluble lead salts. As a rule the iodine value of the mixed "solid" acids, if free from erucic (and gadoleic) acid, will lie in the neighbourhood of 10. In this respect the following table, due to *Tortelli and Fortini*,[4] is instructive :—

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[1] *Arch. d. Pharm.*, 1903, 552.

[2] *Zeits. f. angew. Chem.*, 1904, 1482.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1904, viii. 29.

[4] *Chem. Zeit.*, 1910, 690.

[TABLE

	"Solid" Fatty Acids.	
	Iodine Value.	Melting Point. °C.
Olive oil	7·8	58-59
Rape oil	62·0	41-42
Olive oil, 50 parts Rape oil, 50 parts	32·0	47-48
Olive oil, 70 parts Rape oil, 30 parts	28·0	48-49
Olive oil, 80 parts Rape oil, 20 parts	22·1	50-51
Olive oil, 90 parts Rape oil, 10 parts	12·8	54-55
Sesamé oil	9·3	55-56
Arachis oil	13·0	57-58
Cotton seed oil	19·0	57-58

For purposes of technical examination it is preferable to work with the "solid" acids, instead of the original mixed fatty acids.

Experiments made by the author, with a view to removing the adhering unsaturated fatty acids by converting them into their iodochlorides and separating the latter by crystallisation from the saturated fatty acids, have not led to satisfactory results.

A much more satisfactory method, employed by the author, consists in converting the adhering unsaturated fatty acids by catalytic reduction with hydrogen into saturated acids; in most cases, *i.e.* when oleic, linolic, linolenic, and clupanodonic acids are present, there would be produced stearic acid, the quantitative determination of which can be carried out (see below). If ricinoleic acid be present the product would be hydroxystearic acid or stearic acid (see Chap. III. p. 145); and if erucic acid be present its quantity can be determined as behenic acid.

Determination of Erucic Acid

It has been noted above that the lead salt of erucic acid is sparingly soluble in cold ether; hence if the extraction of the lead salt be carried out with cold ether, the bulk of erucic acid would be found with the solid saturated acid (cp. p. 544). If no other unsaturated acid be present, the determination of the iodine value of the solid acids would furnish an approximate measure of the erucic acid. In consequence of the high prices ruling for linseed oil in the years 1911 and 1912, the problem of detecting rape oil in linseed became prominent, and hence methods of determining erucic acid, the most characteristic acid of rape oil, had gained in importance. Methods for this purpose were proposed by *Holde and Marcusson* on the one hand, and *Tortelli and Fortini* on the other; both methods are very cumbersome and will hardly yield quantitative results.

Tortelli and Fortini [1] saponify 20 grms. of oil in the manner indicated under "lead-salt-ether" method (p. 545), and treat the lead salts in the flask with 20 c.c. of common ether, warming the salts with the ether under a reflux condenser and cooling the corked flask for one hour at exactly 15° C. The clear solution is filtered, care being taken that no solid lead soap is brought on to the filter. The contents of the flask are treated with 40 c.c. of ether under a reflux condenser in a water-bath, the flask is corked and again allowed to stand one hour at 15° C. The solution and the insoluble soap are poured on to the filter through which the first solution has been filtered, and the residue in the flask is transferred on to the filter with the aid of 40 c.c. of ether. Both the "liquid" and the "solid" acids are then isolated in the usual manner, and the "solid" acids examined for the presence of erucic acid by determining the melting point and the iodine value of the "solid" acids, and the "characteristic critical temperature" (Chap. XII.). *Tortelli and Fortini* lay stress on the necessity of using the exact quantity of ether stated above, and of maintaining exactly the temperature of 15° C. for the time stated above. This seems to be very important, as *Holde and Marcusson*[1] state that by prolonged treatment of the lead salt of the fatty acid, the lead salt of erucic acid passes entirely into the ethereal solution. Thus when 3 grms. of the mixed fatty acids of rape oil had been treated with 85 c.c. of dry ether, after standing overnight, only a small quantity of lead salt had remained insoluble. Worse still were the results in the case of a mixture containing 80 per cent of linseed oil and 20 per cent of rape oil.

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[1] *Chem. Zeit.*, 1910, 690.

Holde and Marcusson propose the following process :—

20-25 grms. of the mixed fatty acids are dissolved in double the volume of 96 per cent alcohol, and cooled to − 20° C. in a wide test-tube, whilst the mass is stirred with a glass rod. The residue which separates consists preponderantly of saturated fatty acids ; it is sucked off on a filter at a temperature of − 20° C. and is slightly washed with cooled alcohol. The filtrate is evaporated to dryness and the residue again dissolved in four volumes of 75 per cent (by volume) alcohol, and again cooled to − 20° C. In the presence of erucic acid, after about one hour a crystalline precipitate will settle out, which after sucking off with the aid of a filter-pump and washing with cooled 75 per cent alcohol, is white and consists, to the largest extent, of erucic acid. This is dissolved in warm benzene or ether, the solution is evaporated down, and the mean molecular weight, the melting point, and the iodine value of the fatty acid determined. In case the proportion of erucic acid be very large, part of the erucic acid is found with the saturated fatty acids.

Possibly a combination of the two methods described may lead to better results than each individual method is capable of yielding.

Much better results are obtained by a method worked by the author, details of which have not yet been published. The author reduces either the total mixed acids or the "solid" acids catalytically with hydrogen in the presence of nickel, when erucic acid is converted quantitatively into behenic acid. The importance of the determination of behenic acid will be dealt with in Vol. II. Chap. XIV. "Marine Animal Oils," and Vol. III. Chap. XV. "Hydrogenised Fats."

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[1] *Zeits. f. angew. Chem.*, 1910, 1260.

Since oleic, linolic, linolenic, and clupanodonic acids have been removed as lead salts almost completely by cold ether, the only remaining unsaturated acid would be erucic acid. Its reduction product, viz. behenic acid, could then be determined by the method described below under stearic acid, when (stearic acid and) behenic acid will remain undissolved. The separation of behenic acid from stearic acid may be carried out by crystallisation from alcohol, etc. (see below), but it is sufficient in most cases to determine the mean molecular weight and calculate therefrom the respective amounts of behenic and stearic acids. Any stearic acid present at the outset can be determined as such and accounted for in the final result.

Laboratory apparatus suitable for catalytic hydrogenation has been proposed by *Skita*[1] and by *Voswinckel.*[2]

Solid Saturated Acids

The resolution of the mixed *saturated* fatty acids which occur in the natural oils, fats, and waxes into the individual acids is a very complicated problem, which can only be solved satisfactorily by adopting the strictly scientific methods described in Chapter XII. With regard to *Heintz's* method, described in Chap. XII., it may be pointed out here that it would only seem to apply to a mixture of two fatty acids, as, according to *Holde*,[3] the presence of a third saturated acid of high melting point may lead to uncertain results.

Better results may, however, be expected by converting the fatty acids into their methylesters, and distilling these fractionally (cp. Chap. XII.).

For technical purposes, these methods are too complicated in their present form. Valuable information may, however, be obtained by determining the mean molecular weight of the fatty acids (cp. Chap. VIII. p. 512), and especially the melting point (see Chap. III.). An approximate method of separating the fatty acids of a higher melting point than that of stearic acid is afforded by fractional crystallisation from alcohol. Carnaübic, cerotic, montanic, and melissic acids are practically insoluble in strong alcohol at the ordinary temperature; arachidic acid is sparingly soluble in 90 per cent alcohol, and practically insoluble in 70 per cent alcohol at the ordinary temperature; behenic and lignoceric acids are slightly less soluble than arachidic acid. The acids enumerated here may therefore be separated from the saturated fatty acids lower than stearic acid, and even including stearic acid, by judicious treatment with alcohol. Preliminary experiments made by the author in this direction established the correctness and approximate reliability of the method for the purposes of technical analysis. Such methods are already in use for the detection of stearic acid in the presence of cerotic acid (see Vol. II. Chap. XIV. "Beeswax"), as also for the presence of arachidic acid (see Vol. II. Chap. XIV. "Arachis Oil") in admixture with other acids.

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[1] A. Skita, *Über katalytische Reductionen organischer Verbindungen*, 1912. Stuttgart.

[2] H. Voswinckel, *Chem. Zeit.*, 1913, 489.

[3] *Berichte*, 1905, 1248.

Gsell[1] stated that by treating a mixture of stearic, palmitic, myristic, lauric, capric, caprylic, and caproic acids in dilute ethereal solution with acetyl chloride, the first four acids form their normal anhydrides, viz. stearic, palmitic, myristic, and lauric anhydrides, whereas the last three acids yield mixed anhydrides of acetic acid with capric, caprylic, and caproic acids respectively. On warming the mixture of the normal and mixed anhydrides with pyridine, and pouring the pyridine solution into a large quantity of water, the normal anhydrides, being insoluble in water, separate out, whereas the mixed anhydrides are stated to remain in aqueous solution; hence they can be separated from the undissolved anhydrides. For the further separation of capric, caprylic, and caproic acids by means of their acid chlorides in a 10 per cent solution of methylamine, wherein capric acid is insoluble, and for the subsequent separation of caprylic and caproic acids by means of their strontium salts, the reader must be referred to the original paper.

A confirmation of *Gsell's* statements would seem to be desirable, all the more so as the present author[2] did not obtain a mixed anhydride when treating capric acid with acetic anhydride.

(*a*) *Determination of Behenic Acid*

Behenic acid is characterised by its comparative insolubility in cold alcohol. It would separate out together with stearic acid (see below). Its approximate determination is carried out as indicated under "Determination of Erucic Acid."

(*b*) *Determination of Arachidic Acid*

The approximate determination of arachidic acid (frequently required in the examination of olive oils suspected of containing arachis oil) is carried out by *Renard's*[3] process based on the sparing solubility of arachidic acid in 90 per cent alcohol. The crude arachidic acid so obtained contains lignoceric acid but no stearic acid. The accurate determination of arachidic acid depends on the strict observance of a number of details, which will be fully described in Vol. II. Chap. XIV. under "Arachis Oil." For the detection of arachidic acid in "Hydrogenised Fat" cp. Vol. III. Chap. XV.

(*c*) *Determination of Stearic Acid*

On triturating the mixed fatty acids from a solid fat with dilute alcohol of specific gravity 0·911 in a mortar, the unsaturated fatty acids are almost completely dissolved; palmitic acid is partially dissolved, whereas stearic acid remains almost completely undissolved. In an actual experiment the mixed solid acids so obtained had an iodine value of only 2-3.

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[1] *Chem. Zeit.*, 1907, 100.

[2] Lewkowitsch, *Proc. Chem. Soc.*, 1890, 91.

[3] *Compt. rend.* 73, 1330.

Far better results are obtained in many cases by treating the mixed fatty acids of an oil or fat with an alcoholic solution of pure stearic acid, saturated at 0° C. *Hehner and Mitchell*,[1] proceeding on the lines suggested by *David*,[2] showed by a series of experiments, carried out on pure stearic acid and on mixtures of stearic acid with (*a*) saturated acids lower than palmitic; (*b*) palmitic acid; (*c*) crude oleic acid; (*d*) mixed fatty acids from lard fatty acids, that stearic acid is left undissolved and can be determined quantitatively with accuracy.

Hehner and Mitchell worked with a solution of stearic acid prepared by dissolving about 3 grms. of pure stearic acid in 1000 c.c. of warm (methylated[3]) alcohol of specific gravity 0·8183 (containing 94·4 per cent of alcohol by volume) in a stoppered bottle. The bottle is immersed up to the neck in ice-water (well protected against radiation of heat), and allowed to stand in the ice-water overnight. After twelve hours, the mother liquor is syphoned off—without removing the flask from the ice-water—by means of a small thistle funnel immersed in the alcoholic solution and covered with a piece of fine calico (so as to retain the separated stearic acid crystals in the flask). The funnel is twice bent at right angles, and is best fitted into a suction bottle, so that the clear liquor can be drawn off by means of a filter-pump.

0·5 grm. to 1 grm. of the mixed fatty acids, if solid, or, if liquid, 5 grms., are weighed accurately in a flask and dissolved in 100 c.c. of the above alcoholic stearic acid solution. The flask is placed in ice-water overnight, the mixture is agitated the following morning while the flask is still kept in the ice-water, and allowed to stand for at least half-an-hour in the ice-water in order to promote crystallisation. The alcohol is then filtered off as described above, care being taken to draw off the solution as completely as possible. The residue in the flask is washed three times in succession with 10 c.c. of the alcoholic stearic acid solution, previously cooled to 0° C. The crystals adhering to the calico of the thistle funnel are washed with hot alcohol into the flask, the alcohol is evaporated off, the residue dried at 100° C., and weighed. *Hehner and Mitchell* advise to take the melting point of the acid, which should not be much below 68·5° C. The author considers it necessary, in case the melting point be found too low, to treat the residue once more as described above.

As the walls of the flask and also the undissolved crystals retain a small quantity of the alcoholic stearic acid solution, a correction must be applied, which *Hehner and Mitchell* found in their experiments was 0·005 grm.; this must be deducted from the total weight of the residue found.

The author's earlier experience led him to recommend this method as giving reliable results in the cases represented by the mixtures with which *Hehner and Mitchell* worked. In confirmation thereof the following numbers found in the author's laboratory may be given :—

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[1] *Analyst*, 1896, 321.

[2] *Compt. rend.* 86, 1416; *Journ. Chem. Soc.* 34, 1011.

[3] For reasons given below, methylated spirit should not be used.

Proportion of Stearic Acid in Oils and Fats (*Lewkowitsch*)

	Per cent.
Palm oil, bleached	0·71 ; 0·72
Palm oil, raw (Bassa)	0·53
Butter fat	0·49 [1]
Cocoa nut oil	0·99
Bone fat	2·94
Lard	6-24·91
Tallow, several samples	21-22
Shea butter	33·7-37·3
Cacao butter	39
Surin fat	58·2
Mowrah seed oil	13-25
Illipé oil	12-20

Hehner and Mitchell themselves had shown that this method breaks down with mixtures of Japan wax fatty acids and pure stearic acid. In some cases the latter could only be recovered partially, whereas in other cases none at all was obtained.

More recent experience of the author has shown that this method yields entirely unreliable, or at best capricious results in a large number of cases where mixtures of stearic acid with acids other than palmitic and oleic are present. Even if only palmitic and oleic acids be present in widely different proportions from those found in the oils and fats enumerated in the foregoing table, the results are still very capricious. To take one of many examples, in the case of cotton seed oil fatty acids it was impossible to detect stearic acid by this test, even if 5 or 8 per cent of pure stearic acid had been added to the mixed fatty acids. The same observation has been recorded by *Emerson*.[2] On the author's suggestion, *Emerson*,[3] by means of the lead-salt-ether method, resolved the mixed fatty acids of cotton seed oil into solid and liquid acids. The former gave no crystals in the stearic acid test (cp. Vol. II. Chap. XIV. " Cotton Seed Oil "), but added stearic acid could be recovered, and, curiously enough, more was found than had been actually added.

This last result may be explained by the observation first made by *Kreis and Hafner*[4] (and confirmed by *Emerson*) that stearic acid forms supersaturated solutions (see Chap. III. p. 163). To this cause must be ascribed the fact that *Hehner and Mitchell* found the solubility of stearic acid in alcohol at 0° C. to be much greater than did *Kreis and Hafner* (and *Emerson*), although the employment of methylated spirit by ***Hehner and Mitchell*** may to some extent account for the discrepancy. In the author's experiments pure alcohol of specific gravity 0·8183 was used in order to eliminate such errors as must be caused by the presence of the denaturant in methylated spirit.

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[1] This must not, however, be taken to be stearic acid. The insoluble acids consist probably to some extent of a mixture of arachidic and myristic acids (cp. Vol. II. Chap. XIV. " Butter Fat ").

[2] Private communication.

[3] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, vi, 22.

[4] *Journ. Amer. Chem. Soc.*, 1907, 1751.

Emerson showed that the formation of supersaturated solutions is avoided if the stearic acid solution, required for the determination, is prepared with 7 grams of stearic acid per 1000 c.c. of alcohol (cp., however, p. 163).

This explains satisfactorily why in some experiments the amount of stearic acid found was too high, but it does not explain those cases within the author's experience in which too small an amount of stearic acid, or even none, was obtained. Thus fatty acid mixtures containing, besides stearic acid, large proportions of lauric acid, would not yield any, or at least not the full amount of stearic acid present, even after the "liquid" acids had been removed, or even where supersaturated solutions of stearic acid were used. Again, in other cases within the experience of the author, duplicate experiments made side by side under identical conditions yielded so widely differing results that no reliance whatever could be placed on those determinations. A number of such capricious cases noticed by the author are still under investigation.[1]

Due caution must therefore be observed in the application of this method to the examination of products not specifically mentioned in the foregoing lines; even in some of the cases mentioned there, most capricious results were obtained in duplicate experiments.

A solid acid, even if it have a melting point of 68° C., should not be looked upon as consisting of stearic acid, as of course all higher melting acids (if present), such as arachidic, behenic, etc., will be found in the separated acid (cp. Vol. II. Chap. XIV. "Cotton Seed Oil" and "Arachis Oil"). It is therefore advisable to determine the mean molecular weight of the separated solid acid. The appearance of the crystals also affords some guidance.

(*d*) *Determination of Palmitic Acid*

A direct method for the accurate determination of palmitic acid when in admixture with other solid acids is not yet available. If, however, as is frequently the case, a mixture of stearic and palmitic acids only be given (candle material), its content in palmitic acid can be ascertained by determining the amount of stearic acid as described in the preceding paragraph, and deducting the weight found from the original weight. If the mixed acids contain unsaturated acids, it is necessary to determine the iodine value and calculate to oleic acid; in most cases this will be sufficiently accurate (see below). Less accurate numbers is the calculation of the proportions of the two acids from the mean molecular weight of the mixed acids, in the manner shown in Chapter XI.

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[1] Cp. also Berg, *Chem. Zeit.*, 1908, 777.

A method, suggested by *Kreis and Hafner*, for the separation of palmitic acid from stearic acid will be described in Chapter XII.

7. Determination of Oleic Acid in the absence of other Unsaturated Fatty Acids

If the insoluble fatty acids contain no other unsaturated acids than oleic acid, then its quantity can be calculated from the iodine value of the mixed fatty acids, as shown above (p. 542). If a mixture of oleic, palmitic, and stearic acids be given, each component of the mixture can be determined quantitatively as follows: Let I be the iodine value of the mixed fatty acids. The percentage of oleic acid, x, is then found as follows :—

$$90{\cdot}07 : 100 : : I : x \; ; \; x = \frac{100\,I}{90{\cdot}07} = 1{\cdot}1102\,I.$$

The proportion of stearic acid is next ascertained by the method described above. By deducting the sum of the percentages of oleic acid and stearic acid, the proportion of palmitic acid is found ; the identity of this acid should also be established. The calculation from the iodine value and the mean molecular weights, as illustrated by the example given in Chapter XI., would be less accurate.

Less accurate still is a method (*David*[1]) based on the greater solubility of oleic acid in a mixture of alcohol and acetic acid as compared with the solubility of palmitic and stearic acids. This method was described in the second edition of this work, p. 197.

8. Detection, Separation, and Approximate Determination of Individual Liquid Fatty Acids — Oleic, Linolic, Linolenic, Clupanodonic

In a preliminary operation the " liquid " fatty acids must be separated from the " solid " acids by the lead-salt-ether method. The author recommends the following *modus operandi* :—The quantity of liquid fatty acids is first determined approximately in 3 to 4 grms. of the mixed fatty acids or of the original oil by the method described p. 545. Then, in a fresh experiment, a larger quantity of liquid fatty acids is prepared by *Tortelli and Ruggeri's* method.

The next step is to determine the iodine value of the isolated liquid acids, so as to gain a preliminary insight into their composition. This will be readily obtained by referring to the table given in Chapter VI. p. 406, and in this chapter, p. 539, and by consulting the following table, in which I collate the iodine values of the liquid fatty acids derived from a number of commercial oils and fats :—

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[1] *Compt. rend.* 86, 1416.

Iodine Values of Liquid Fatty Acids derived from

Oil.	Class of Oil.	Group.	Iodine Value.
Linseed . . .	Drying oils		190-209·8
Tung, Chinese . .			179·7
Candle nut . . .			185·7
Stillingia . . .			178·1-191
Cedar nut . . .			184
Walnut . . .			167
Safflower . . .			140·5-159·6
Soya bean . . .			131 (?)
Poppy seed . . .			150
Manihot . . .			163·6
Millet seed . . .			146·3
Niger seed . . .			147·5
Sunflower . . .			154·3
Para rubber seed . .			154·2
Raspberry seed . .			185·9
Blackberry seed . .			163·2
Red Currant . .			190·1
Cameline . . .	Semi-drying oils	Cotton seed oil group	165·4
Grape seed . . .			151·7
Maize (corn) . .			140-144
Persimmon seed . .			131·5
Cotton seed . . .			147-151
Sesamé . . .			129-139·9
Sorghum . . .			148·1
Ravison . . .		Rape oil group	124·2
Rape (colza) . .			121-125
Black mustard seed .			119·8
White mustard seed .			103 1
Quince . . .	Non-drying oils		132·1
Cherry kernel . .			124·7
Apricot kernel . .			111·5
Plum kernel . .			98·6-102·2
Peach kernel . .			101·9-104·1
Almond . . .			101·7
Arachis . . .			105-128
Rice			130·7
Tea seed . . .			99·6-104·4
Tsubaki . . .			89
Sasanqua . . .			92·9
Pistachio . . .			105·8
Hazel nut . . .			91·3-98·8
Elderberry . . .			120
Olive			93-112
Calophyllum . .			114·5
Senega root . . .			82·4
Secale			104
Canari			110·4
Castor		Castor oil group	106·9

Iodine Values of Liquid Fatty Acids derived from—continued

Oil or Fat.	Class of Oil or Fat.	Group.	Iodine Value.
Salmon	Marine animal oils	Fish oils	197·4
Cod liver		Liver oils	
Whale		Blubber oils	144·7
Chrysalis	Terrestrial animal oils		178·73
Tallow oil			92·2-92·7
Lard oil			
,, ,, (European)			95·2-96·2
,, ,, (American)			103-105
Carapa	Vegetable fats		108
,, grandiflora			94·7
Nux vomica			94-96·2
Baobab			97·6
Niam			134·5 ; 139
Palm			94·6-99
Akee			82·4
Macassar			103·2
Nutmeg butter		Myristica group	93·5
Vegetable tallow			97·04
Palm kernel		Cocoa nut oil group	44-48[1]
Cocoa nut			22-32[1]
,, oleine			36·3[1]
Human fat	Animal fats		92·1
Lard (European)			92·1-104
,, (American)			92-115
Beef tallow			92·4
Mutton tallow			92·7

Wallenstein and Finck[2] proposed to term the iodine value of the liquid fatty acids the "inner" or "absolute iodine number" of the oil. As it appears undesirable to multiply the number of terms that require a definition, I shall adhere in this work to the denomination "iodine value of the liquid fatty acids."

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[1] The low iodine values are, of course, due to the presence of saturated fatty acids of low molecular weight, the lead salts of which are soluble in ether.

[2] *Journ. Soc. Chem. Ind.*, 1895, 78.

(*a*) *Mixture of Oleic and Linolic* (*Elæomargaric, Elæostearic*) *Acids*

If the mixed liquid fatty acids consist of oleic and linolic acids only, their respective quantities in the mixed liquid fatty acids can be calculated, and by referring these quantities to the amounts of original mixed fatty acids, or original oil or fat, the absolute quantity of oleic and linolic acids can be ascertained. The assumption that these two unsaturated acids alone need be considered will most frequently hold good in those cases where the absence of linolenic acid has been proved by one of the methods described below. Let x be the proportion of oleic acid and y the proportion of linolic (elæomargaric) acid, and I the iodine value of the mixed liquid fatty acids. Since the theoretical iodine values of oleic and linolic acids are 90·07 and 181·42 respectively, we have the following two equations :—

$$x+y=100,$$

$$\frac{90{\cdot}07x}{100}+\frac{181{\cdot}42y}{100}=I.$$

From these two equations x and y can be calculated, and, as mentioned already, the figures so obtained may be referred to the total mixed fatty acids or to the original oil or fat.

The calculation of the respective quantities of oleic and linolic acids from their neutralisation numbers or their mean molecular weights would in this case obviously lead to unreliable results, since their respective molecular weights, 282 and 280, lie very near to each other (cp. Chapter XI.).

(*b*) *Mixture of Oleic, Linolic, Linolenic, and Clupanodonic Acids*

The detailed examination of the liquid fatty acids is somewhat complicated. *Hazura's* [1] investigations suggest the application of the following two methods :—1. Detection and identification of the liquid fatty acids by means of their oxidation products. 2. Identification of the liquid fatty acids by means of their bromo-derivatives. The first method refers to oleic, linolic, and linolenic acids only, as the oxidation products of clupanodonic acid have not yet been studied.

1. *Isolation of the Oxidation Products of the Liquid Fatty Acids*

This method is based on the oxidation of the liquid fatty acids by means of a dilute alkaline solution of potassium permanganate. *Hazura and Grüssner* stated, as the outcome of *Saytzeff's* and their own researches, the following general rule :—All unsaturated fatty acids, when oxidised with potassium permanganate in dilute alkaline solution,

[1] *Monatsh. f. Chem.*, 1887, 147 ; 156 ; 260. 1888, 180 ; 190 ; 469 ; 478 ; 944 ; 947. 1889, 190.

have as many hydroxyl groups added as there are unsaturated valencies in the molecule, and yield as oxidation products saturated hydroxylated acids containing the same number of carbon atoms. A list of the hydroxylated fatty acids obtained by this method has been given already in Chapter III. p. 224, followed by a description of the individual hydroxylated acids. In the examination of the majority of drying oils the oxidation products of oleic, linolic, and linolenic acid(s), viz. dihydroxystearic, sativic, and linusic (isolinusic) acids, must be expected.

It has not yet been decided experimentally whether clupanodonic acid yields hydroxylated acids; it would appear, however, that clupanodonic acid does not conform to the above rule, being broken down to lower fatty acids.

The oxidation process is carried out in the following manner:—30 grms. of liquid fatty acids are neutralised with 36 c.c. of caustic potash of 1·27 specific gravity. The resulting soap is dissolved in 2000 c.c. of water, and an equal volume of a 1½ per cent solution of potassium permanganate is added in a thin stream with constant stirring. The solution is allowed to stand for ten minutes, and as much of a sulphurous acid solution added, with continuous agitation, as will dissolve all the precipitated hydrated manganese peroxide, and impart to the solution an acid reaction. *Dihydroxystearic* and *sativic* acids are precipitated (A), whereas *linusic* and *isolinusic* acids remain dissolved (B).

The precipitated acids (A) are first washed with a little ether, in order to remove some of the original liquid acids that have escaped oxidation, and then extracted with large quantities of ether at the ordinary temperature, 2000 c.c. of ether being used for every 20 grms. of the precipitate. The *ethereal solution*, containing dihydroxystearic acid, is evaporated down to 150 c.c.; on cooling, crystals are obtained which, after recrystallisation from alcohol, can be identified as *dihydroxystearic* acid by their habitus, melting point, molecular weight, and acetyl value. The portion which is found to be insoluble in the cold ether is boiled out repeatedly with large quantities of water.[1] Each quantity is filtered off hot and allowed to deposit crystals on cooling. Each crop of crystals is examined separately. *Sativic* acid can be identified by its melting point and crystalline form. Any insoluble acid represents dihydroxystearic acid which had not been dissolved by ether.

The acid filtrate (B) is neutralised with caustic potash, boiled down to one-twelfth or one-fourteenth of its original volume, and acidulated with sulphuric acid. The precipitate, consisting of a brown flocculent mass, is dried by exposure to the air and treated with ether, which dissolves azelaïc acid and other secondary acidic products of oxidation. The insoluble portion is then crystallised, first from alcohol and then from water. *Isolinusic* and *linusic* acids are recognised by their melting points and crystalline forms; isolinusic acid presents under the microscope characteristic needles, and linusic acid obtruncated rhombic plates. To effect a separation of the more soluble isolinusic acid from the less soluble linusic acid, the mass is recrystallised from a moderate quantity of water. By weighing the several acids thus obtained, the quantitative composition of the liquid acids may be estimated approximately.

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[1] H. Meyer and A. Eckert (*Monatsh. f. Chem.*, 1910 (31), 1243) consider this procedure as too cumbersome, and prefer to extract with hot 30 per cent alcohol, from which considerable quantities of acid separate out on cooling.

A synopsis of the preceding operations is given by the author in the following table :—

Hydroxylated Acids

A. Precipitate.		B. Filtrate.	
a. Soluble in Ether.	b. Insoluble in Ether.	a. Easily Soluble in Water.	b. Sparingly Soluble in Water.
Dihydroxystearic acid.	Sativic acid	Isolinusic acid	Linusic acid

The following table summarising some of the properties of the four acids and their barium salts, has been compiled by the author, so as to assist the reader in mapping out another method of separation :—

Acid.	Formula.	Melting Point. °C.	Solubility of the						
			Acids in					Barium Salts in	
			Water.		Alcohol.		Ether.	Water.	
			Cold.	Hot.	Cold.	Hot.		Cold.	Hot.
Dihydroxystearic .	$C_{18}H_{34}O_2(OH)_2$	137	Insoluble	Insoluble	Sparingly soluble	Soluble	Sparingly soluble	Insoluble	Insoluble
Sativic . . .	$C_{18}H_{32}O_2(OH)_4$	173	Insoluble	Sparingly soluble	Sparingly soluble	Soluble	Insoluble	Insoluble	Insoluble
Linusic . . .	$C_{18}H_{30}O_2(OH)_6$	203–205	Sparingly soluble	Soluble	Sparingly soluble	Sparingly soluble	Insoluble	Sparingly soluble	Readily soluble
Isolinusic . .	$C_{18}H_{30}O_2(OH)_6$	173–175	Sparingly soluble	Readily soluble	Soluble	Soluble	Insoluble	Sparingly soluble	Readily soluble

In the case of cod liver oil fatty acids, *Heyerdahl* found that, under the conditions described above, oxidation proceeds too far, no more than 2 grms. of hydroxylated acids having been recovered from 50 grms. of crude acids. (Evidently the clupanodonic acid in cod liver oil is very readily broken down to fatty acids of lower molecular weight.) Good results, however, were obtained when the oxidation was carried out with a half-saturated solution of potassium permanganate at the temperature of the freezing point [1] of water.

For the oxidation of unsaturated fatty acids of high molecular weight, such as erucic (and brassidic) acid, a large excess of caustic potash must be used.

The foregoing method can only be employed as a qualitative one, since oxidation proceeds beyond the stage of hydroxylated acids, dibasic acids and aldehydes being formed. The method will be found especially useful, if it be desired to prove the presence of oleic acid by isolating the dihydroxystearic acid thus obtained.

The application of the oxidation method to the *total mixed* liquid fatty acids (consisting of a mixture of oleic, linolic, and linolenic acids) is, however, not advisable, as the less saturated fatty acids are attacked first and a considerable quantity of oleic acid escapes oxidation.[2] Thus *Hazura* found in the mixed liquid linseed fatty acid, judging from the amount of dihydroxy acids obtained by oxidation, 4·5 per cent of oleic acid only, whereas *Fahrion* obtained by the same method a much larger yield of dihydroxystearic acid, leading to about 15-20 per cent of oleic acid, he having first separated off the *bulk of* linolic and linolenic acids by a method simulating the oxygen absorption method (impregnation of chamois leather with oil) described in Chap. VII. p. 474.

This method [2] consists in impregnating purified cotton wool (cp. "Wool Oils," Vol. III. Chap. XV.) with the mixed fatty acids and exposing the material for a period of fourteen days to the atmosphere, the material being frequently turned over. The material is then treated with alcoholic potash and the unoxidised fatty acid is separated off by the method described under "Oxidised Fatty Acids" (Chap. VIII. p. 581). The fatty acids soluble in petroleum ether are then separated by the lead-salt-ether method into solid and liquid acids. The latter consist preponderantly of oleic acid and smaller quantities of less saturated acids, the quantity of which can be ascertained approximately by determining the iodine value of the liquid fatty acids and applying the bromination method (see below).

The dihydroxystearic acid obtained by oxidising the liquid acids may be calculated to oleic acid, bearing in mind, however, that even pure oleic acid yields only about 60 per cent of dihydroxystearic acid (cp. p. 182).

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[1] Cp. also Bedford, *Inaug. Dissert.*, Halle a/S, 1906 ; Kržižan, *Chem. Revue*, 1908, 7.

[2] Fahrion, *Zeits. f. angew. Chem.*, 1910, 722 ; 1108.

For the detection of linolic, linolenic, and clupanodonic acids the bromination method will be found preferable.

2. *Isolation and Determination of the Bromo-derivatives of Liquid Fatty Acids*

The method described in the following lines is based on the different solubilities of the several bromo-derivatives. It will be best followed by examining the following table, in which I collate our present knowledge of the bromides of the unsaturated fatty acids, having sixteen to twenty-two carbon atoms in their molecule.

Bromo-derivatives of Unsaturated Fatty Acids

Bromo-derivative from	Name of Acid.	Formula.	Molecular Weight.	Melting Point.	Containing Bromine.	Solubility in						
				°C.	Per cent.	Alcohol.	Ether.	Chloroform.	Petroleum Ether.	Benzene.	Glacial Acetic Acid.	Carbon Tetrachloride.[1]
Hypogæic acid	Dibromopalmitic Hypogæic dibromide	$C_{16}H_{30}O_2Br_2$	414	29	38·66			Easily soluble				
Oleic acid .	Dibromostearic Oleic dibromide	$C_{18}H_{34}O_2Br_2$	442	Oil	36·18	Readily soluble	Readily soluble	Readily soluble	Readily soluble	Readily soluble	Readily soluble	
Elaïdic acid .	Dibromoelaïdic Elaïdic dibromide	$C_{18}H_{34}O_2Br_2$	442	27	36·18							
Erucic acid	Dibromobehenic Erucic dibromide	$C_{22}H_{40}O_2Br_2$	496	46-47	32·26			Easily soluble				
Brassidic .	Dibromobrassidic Brassidic dibromide	$C_{22}H_{40}O_2Br_2$	496	54	32·26							
Linolic acid [2] .	Tetrabromostearic Linolic tetrabromide	$C_{18}H_{32}O_2Br_4$	600	113-114	53·33	Easily soluble	Easily soluble	Easily soluble	*Sparingly soluble*	Easily soluble	Easily soluble	
Tariric acid .	Tariric dibromide	$C_{18}H_{32}O_2Br_2$	440	32	36·37							
Tariric acid .	Tariric tetrabromide	$C_{18}H_{32}O_2Br_4$	600	125	53·33							
Telfairic acid	Telfairic tetrabromide	$C_{18}H_{32}O_2Br_4$	600	57-58	53·33	Easily soluble						
Linolenic acid	Hexabromostearic Linolenic hexabromide	$C_{18}H_{30}O_2Br_6$ . .	758 . .	180-181[3]	63·32	Very sparingly soluble	Very sparingly soluble [4] in the cold	Soluble	Almost insoluble	Soluble	Very sparingly soluble	Soluble in the hot [1]
Clupanodonic acid . .	Octobromo-stearic Clupanodonic octobromide	$C_{18}H_{28}O_2Br_8$	916	. . [5]	69·87		Very sparingly soluble even in the hot					Sparingly soluble in the hot [1]
Arachidonic acid . .	Octobromo - arachidic	$C_{20}H_{32}O_2Br_8$	944	. . [6]	67·8		Insoluble in all organic solvents					
Hydroxy acid in Quince oil		$C_{18}H_{34}O_3Br_2$	458	108	34·91	. .	. .	. .	Soluble			
Ricinoleic .	Dibromoricinoleic Ricinoleic dibromide	$C_{18}H_{34}O_3Br_2$	458	Oil	34·91	Soluble	Easily soluble					
Ricinelaïdic .	Dibromoricinelaïdic Ricinelaïdic dibromide	$C_{18}H_{34}O_3Br_2$	458	Oil	34·91							

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[1] See the author's observations under "Marine Animal Oils" in Vol. II. Chap. XIV.; on cooling, the hexabromides separate in a crystalline form, whereas the octobromides separate in a gelatinous form.

[2] For a second linolic tetrabromide melting at 56°-57° C. see p. 199.

[3] Rollett finds even 181°-182° C. after recrystallisation from benzene (*Zeits. f. phys. Chem.*, 1909 (62) 424). Eibner and Muggenthaler (see p. 573) consider 177° as the correct melting point.

[4] Treatment with ethyl acetate at a temperature of 55°-60° C. is recommended by Bedford.

[5] Blackens at 200° C. and decomposes on further heating.

[6] Blackens at 220° C. and decomposes on further heating.

The bromination test can be applied to the total mixed fatty acids without it being required to separate the "solid" from the "liquid" acids. The mixed fatty acids are brominated in the same manner as has been described above in the bromide test (cp. Chap. VII.) :—0·3 grm. of the fatty acids are dissolved in glacial acetic acid, and the solution is cooled in a corked flask to 5° C. The further treatment is identical with that described p. 476.[1]

The ether-insoluble bromo-derivatives consist either of octo-bromide or of hexabromide or of a mixture of both. An octobromide is characteristic of fish, liver, and blubber oils, whereas a hexabromide is characteristic of vegetable drying oils.

For the quantitative determination *Hehner and Mitchell* recommended to remove completely any dibromide, and then to determine the proportion of bromine in the *crude* bromo product, which in the case of vegetable drying oils would consist of a mixture of hexabromide and tetrabromide. Since a hexabromide contains theoretically 63·32 per cent of bromine, and a tetrabromide 53·33 per cent, the respective amounts of acids can be calculated from the following two equations :—

$$x+y=100,$$

$$\frac{63{\cdot}3x}{100}+\frac{53{\cdot}3y}{100}=\mathrm{B},$$

in which x is the percentage of hexabromide, y the percentage of tetrabromide, and B the percentage of bromine in the crude bromides.

The following table contains a number of determinations of ether-insoluble bromides from mixed fatty acids (cp. also Vol. II. Chap. XIV. "Marine Animal Oils"), carried out according to the above described method :[2]—

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[1] Cp. also Tsujimoto, *Journ. College Engin.*, Tokyo, 1906, vol. iv. 1. ; Procter and Bennett, *Journ. Soc. Chem. Ind.*, 1906, 800 ; Halphen, *Bull. Soc. Chim. de France*, 1907 (iv.), 1, 230. The modifications suggested by Procter and Bennett are considered as superfluous by L. M. Tolman (*Journ. Ind. and Eng. Chem.*, 1909, 341).

[2] Cp. Vol. II. Chap. XIV. "Perilla Oil."

[TABLE

	Kind of Oil.	Yield of Ether-insoluble Bromide from Fatty Acids. Per cent.	Observer.
Hexabromide .	Perilla	53·3 [1]	Meister
	Linseed (iodine value = 181)	29·06 ; 29·34	Walker and Warburton[2]
	,, (iodine value = 184)	31·31 ; 30·44 ; 30·80	,, ,,
	,, (iodine value = 190·4)	38·1 ; 42·0	Lewkowitsch
	,, liquid acids (iodine value = 208) .	34·9	Walker and Warburton[2]
	Candle nut . . .	11·53 ; 11·23 ; 12·63	,, ,,
	Stillingia	25·78	,, ,,
	Para rubber seed . .	6·66	Menon,[2] Link [2]
	Safflower	1·65 ; 0·65	Walker and Warburton[2]
	Soya bean [3] . . .	5·1	,, ,,
	Rape	2·4 ; 3·4	,, ,,
Octobromide .	Japan fish (old sample) .	23·04 ; 23·32	,, ,,
	,, (fresh samples) .	44·2 ; 47·1	Tsujimoto
	Deodourised fish . .	38·42 ; 39·27	Walker and Warburton[2]
	Cod liver, Norwegian . .	29·86 ; 30·36	,, ,,
	Newfoundland cod . .	39·1 ; 37·76	,, ,,
	Shark liver . . .	12·68 ; 15·08	,, ,,
	Seal	19·83 ; 19·93	,, ,,
	Whale (old sample . .	12·38 ; 12·44	,, ,,
	,, (fresh samples) .	22·59 ; 27·77	Lewkowitsch
	,, (fresh sample) .	27·81	Tsujimoto
	Herring	12·7 ; 21·7	,,
	Sperm	2·05	Walker and Warburton[2]

It has been pointed out already above (see p. 478) that the bromide test is best carried out with the fatty acids and not with the glycerides. It may further be added that the hexabromides of the fatty acids crystallise well and hence are easily filtered. The octobromides are, as a rule, amorphous and fall out in flocks, and hence are less easily filtered. (It is therefore advisable to use a paper filter and not an asbestos plug; see below.) Thus a mere inspection of the precipitate, whether crystalline or not, gives some preliminary clue.

The following solubilities of octobromide and hexabromide were determined in the author's laboratory:—

Octobromide (prepared from whale oil) was treated with an excess of boiling, crystallisable benzene which was filtered off hot. 100 c.c. dissolved 0·1984 grm. of octobromide.

Hexabromide.—100 c.c. of crystallisable benzene dissolved at 60° F. 0·024 grm. of hexabromide melting at 181° C. The dissolved hexabromide recovered from 25 c.c. of benzene melted at 174° C.

100 c.c. of boiling benzene, quickly filtered off from an excess of hexabromide melting at 181° C. (from linseed oil), dissolved 0·7288 grm. The crystals recovered from the mother liquor of the boiling benzene melted at 180° C.

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[1] Cp. Vol. II. Chap. XIV. "Perilla Oil."

[2] These determinations were carried out in the author's laboratory.

[3] In case of soya bean oil three hours standing in the cold gave no precipitate of hexabromide, but when standing over night in the cold hexabromides were obtained. Hence standing for more than three hours is necessary in the case of oils containing small quantities of linolenic acid.

It must, however, be pointed out that the numbers found above for the separate bromides do not apply to a mixture of octobromide and hexabromide. The separation of mixed hexabromide and octobromide can, however, be carried out completely. Experiments showed that the hexabromide separated from octobromide by means of benzene exhibited no trace of blackening in the melting-point test.

The above described method for determining the hexabromides does not furnish the full yield of hexabromides formed. In the solution of tetrabromide, or of tetrabromides and dibromides, certain quantities of hexabromides remain dissolved. They are recovered by further crystallisation from the mother liquor, either by allowing to stand or after slight concentration of the solution by distilling off a portion of the ether. Thus, in the examination of a linseed oil, the author obtained by subsequent concentration of the mother liquors the following figures :—

	Per cent.
Insoluble bromide of m.p. 182°	35·11
„ „ „ 170°	6·15
„ „ „ 165°	2·11

In addition thereto, by further concentration of the mother liquors, lower fractions melting respectively at 150° and 135° C. were obtained ; their quantities were, however, very small. All the hexabromide appeared to have been recovered with the last fraction melting at 135° C., inasmuch as the *tetrabromide* recovered from the mother liquor by the process described below, had the correct melting point of 113°-114° C.

In another specimen of linseed oil fatty acids the following results were obtained (*Menon* [1]) :—

		Per cent.
Hexabromide of m.p.	181° C.	39·37
Bromides of m.p.	151° C.	3·09
„ „	140° C.	7·83
„ „	135°-136° C.	2·38

The proportion of unsaponifiable matter left in the mixed fatty acids also influences the result to a notable extent. This will be gathered from the following table detailing the examination of a linseed oil fatty-acid, carried out by the author :—

Hexabromide Test of Linseed Oil

	Fatty Acids retaining Unsaponifiable Matter.		Fatty Acids freed from Unsaponifiable Matter.	
	Per cent.	m.p. ° C.	Per cent.	m.p. ° C.
Hexabromide				
1st crystallisation . . .	26·44	183	28·52	183
2nd „ . . .	5·07	180	3·54	180
Bromide from petroleum ether	11·37	168	5·48	171

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[1] Determined in the author's laboratory.

The incomplete recovery of the hexabromide by the above described method would seem to be due to the employment of acetic acid and to unfavourable conditions as regards temperature and concentration.

An exhaustive study of the bromide test as applied to vegetable drying oils has been made recently by *Eibner and Muggenthaler*.[1] They ascertained that the more glacial acetic acid is used, the lower is the yield of hexabromide, and that glacial acetic acid produces impure (grey) hexabromide. The best temperature at which the highest yield of hexabromide could be obtained was found to be -10° C., when using a concentration of 10 per cent fatty acid in ethereal solution. Under these conditions no such after-precipitation, as was observed by the author in the above given example, took place. The amount of bromine required for complete precipitation of the bromide was 1 c.c. of bromine for 2 grms. of fatty acids dissolved in 20 c.c. of ether.

The following *modus operandi* is recommended by *Eibner and Muggenthaler* :—2 grms. of mixed fatty acids (for the preparation of which the authors give unnecessarily elaborate details) are dissolved in a flask in dry ether to a 10 per cent solution, and cooled down to -10° C.; then 0·5 c.c. of bromine is allowed to run into the solution from a very finely drawn out pipette, the time allowed for this being about twenty minutes.

The remainder of 0·5 c.c. of bromine is added somewhat more rapidly, within about ten minutes, the bromination thus occupying about thirty minutes. The authors attach great value to the exact observance of the time. The temperature should never be allowed to rise during bromination above -5° C. The flask is then corked and allowed to stand for two hours at -10° C. The ethereal solution is next decanted through a weighed asbestos filter (in the writer's opinion a paper filter is better) and the precipitate is washed with five lots of 5 c.c. each of dried and cooled ether. After complete draining the precipitate is dried for two hours at 80° to 85° C., and allowed to cool in a desiccator. The temperature is designedly kept below 100°, as the authors found that the colour of the hexabromide becomes somewhat grey if the drying takes place at 100°. The melting point of the hexabromides was 177°, whereas (see Chapter III. p. 207) the melting point of pure hexabromide has been found to be higher. No doubt the low melting point is due to the drying having been carried out below 100° C.

Nevertheless small traces of retained moisture cannot account for the much larger yield of hexabromide which the authors obtained.

The yields of hexabromide obtained by these authors is tabulated here :—

Fatty Acids from	Per cent.
Perilla oil	64·12
Linseed oil, Baltic	57·96
Linseed oil, Dutch	51·73

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[1] *Farben-Zeitung*, 1912, No. 3 ff.; H. Muggenthaler, *Inaug. Dissert.*, 1912. Augsburg.

Fatty Acids from	Per cent.
Linseed oil, La Plata	51·66
Linseed oil, Indian	50·50
Tung oil	nil
Soya bean oil	up to 7·78
Poppy seed oil	nil
Rape oil	6·34

Further investigations must show how far the foregoing results affect the theoretical deduction of *Rollett*, as regards the yield of the crystalline hexabromide (see Chap. III. p. 207).

The mother liquor from the ether-insoluble hexabromide or octobromide (or mixed octo- and hexabromide) contains tetrabromide and dibromide. As will be gathered from the table p. 569, the different solubilities of oleic dibromide and linolic tetrabromide suggest a method of separation. Oleic dibromide is readily soluble in petroleum ether of boiling point 35°-67·5° C., whilst linolic tetrabromide dissolves in it with great difficulty and on boiling only, separating out again in very fine, long, lustrous needles on cooling. 100 c.c. of petroleum ether at 12° C. hold in solution 0·014 grm. to 0·021 grm. of linolic tetrabromide, and less still at lower temperatures (*Farnsteiner*). Experiments instituted with weighed quantities showed, however, that a smaller quantity than 4-5 per cent of linolic acid could not be isolated from a mixture of linolic and oleic acids.

Determinations made in the author's laboratory showed that 100 c.c. of petroleum ether (spec. grav. 0·6375) dissolved at 60° F. 0·0264 grm. of a pure tetrabromide (from cotton seed oil) melting at 114° C. 100 c.c. of the same petroleum ether dissolved at its boiling point (80° F.) 0·172 grm. The undissolved portion melted at 115° C., whereas the crystals recovered from the dissolved portion melted at 113°. This proves incidentally the purity of the original tetrabromide.

The mother liquor from the filtered ether-insoluble bromides contains an excess of bromine. It is best to wash the ethereal solution in a separating funnel with sodium thiosulphate to remove the free bromine. The washed bromides are then dissolved in ether, the adhering water is drained off, and the last traces of water are removed by filtering through a dried filter.

The ether is distilled off and the residue boiled with sufficient petroleum ether to dissolve it completely. On cooling, the crystalline bromide melting at 114° C. separates out.

It has been pointed out in Chapter III. that there is also in existence a second linolic tetrabromide, melting at 56° C. This has hitherto only been met with in isolated cases.

In the following table I collate the proportions of linolic acid found by *Farnsteiner*. In the case of cotton seed oil, the percentage of linolic acid has been confirmed by determinations made in the author's laboratory.

Oil or Fat.	Linolic Acid calculated from separated Tetrabromide.	Remarks.
	Per cent.	
Cotton seed oil . . .	18·5	
Sesamé oil	15·8-12·6	
Rape oil	...	Linolenic acid present
Mustard oil	4·5	4 per cent of linolenic acid
Almond oil	5·97	
Arachis oil	6·0	
Olive oil	Small quantity	
Horse fat	9·9	
Lard (European) . . .	Small quantity	Traces of linolenic acid present
Tallow	...	,, ,, ,,
Butter fat[1]	...	,, ,, ,,

It will be seen that the proportions of linolic acid, as stated in the last table, are much lower than would be calculated from the iodine values. This may perhaps be explained by *Rollett's* theory (see Chap. III. p. 198). With a view to testing this point the following experiments were carried out (with the assistance of *Menon*, *Link*, *a. o.*) in the author's laboratory. They must, however, be considered as being yet too incomplete to admit of any generalisation.

Soya bean oil yielded in the bromide test:

	Per cent.
Hexabromide, m.p. 179° C.	5·07
Tetrabromide, m.p. 113·5° C.	19·92

corresponding to

Linolenic acid	1·85
Linolic acid	9·28

After distilling off half the amount of petroleum ether from the mother liquor and exposing the solution to a temperature of about 5° C., further 25·04 per cent of tetrabromide (melting at 113° C.), corresponding to 11·66 per cent of linolic acid, were obtained. Hence a total of 20·94 per cent of linolic acid was found.

Maize oil fatty acids gave in the bromide test, in three successive crystallisations from petroleum ether, the following amounts:

	Per cent.
I. Tetrabromide, melting at 113° to 114° C.	50·87
II. ,, ,, 113° C.	6·98
III. ,, ,, 113° C.	3·16
	61·01

corresponding to 28·43 per cent of linolic acid.

These results must, however, not be taken as typical, since slight changes in temperature and amount of petroleum ether used affect the yield considerably. Thus, in a second experiment with maize oil fatty acids, there were obtained in the first crystallisation 30·78 per cent of tetrabromide, melting at 113·5° C.; and after distilling off from the filtrate two-thirds of the petroleum ether and exposing the flask to a temperature about 5° C., no crystals appeared. Even after distilling one-half of the petroleum ether off the already concentrated solution, no crystals were obtained immediately; after prolonged cooling at 3-5° C., 3·56 per cent more tetrabromide was obtained. Hence this duplicate test yielded only 34·34 per cent. The 3·56 per cent of crystals melted at 61° C. The quantity was too small to decide whether the crystals represented a mixture of the two tetrabromides melting at 114° and 56° C. respectively.

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[1] The cows yielding this specimen of butter fat having been fed a long time on cotton seed cake, the linolenic acid found may be due to cotton seed oil (cp. Vol. II. Chap. XIV. "Butter Fat").

Cotton seed oil fatty acids yielded 51·85 per cent of tetrabromide (melting at 112° C.), corresponding to 24·93 per cent of linolic acid. After concentrating the mother liquor a further crop of 6·5 per cent of tetrabromide, corresponding to 2·9 per cent linolic acid, was obtained. Yet in other sets of experiments by other observers no more than 17·8 per cent was collected in two crystallisations.

Sesamé oil fatty acids gave 6·48 per cent of tetrabromide melting at 113° C.; a second crop yielded 6·48 per cent (melting at 113° C.), and a third crop gave 2·6 per cent of tetrabromide, melting at 111° C. There were therefore obtained:

	Per cent.
First crop	24·5
Second crop	6·48
Third crop	2·6

= 33·58 per cent of tetrabromide, corresponding to 15·62 per cent of linolic acid. *Farnsteiner* (see above table), however, obtained this yield in one operation.

The author suggests to combine the methods described above in a systematic examination in the following manner: [1]—

Resolve the mixed fatty acids into "solid" fatty acids and "liquid" fatty acids. (Inasmuch as the unsaponifiable matter in some cases contains a high proportion of unsaturated substances (cp. Chap. XII.) which absorb bromine, it is advisable in accurate analysis to remove the unsaponifiable matter first.) The liquid fatty acids are then brominated in ethereal solution. Pending the confirmation of the results obtained by *Eibner and Muggenthaler*, it would seem to be advisable to carry out the bromination in dry ethereal solution as directed by these observers. The precipitated ether-insoluble bromides are washed with ether and examined separately.

A preliminary examination, after weighing the ether-insoluble bromide, consists in determining the melting point. If the bromides melt to a clear liquid without showing signs of blackening at or about 180°, then the absence of octobromide is proved. It cannot, however, be concluded that hexabromide is absent. Further preliminary information may be obtained by determining the bromine content of the mixed ether-insoluble bromides. It is, however, more expedient to proceed at once to the separation by means of boiling benzene. The solubilities given above for the hexabromides and octobromides in benzene, show that the undissolved portion will be rich in octobromide, whereas the filtrate consists practically of hexabromide. A further examination by the melting point test of the insoluble portion will confirm the presence of octobromide and will show whether any hexabromides are present; in that event, the filtrate, after evaporating off the benzene, yields crystals melting at 180° to a clear liquid, without blackening.

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[1] Cp. *Jahrbuch der Chemie*, 1898 (viii.), 402.

The quantitative determination of both the undissolved octobromide and the residue obtained after evaporating the benzene from the solution will hardly yield sufficiently accurate quantitative results.

It would therefore be preferable in accurate determination to estimate the bromine contents of both the undissolved and the dissolved portions in addition to the bromine determination of the total insoluble bromides.

The ethereal solution, after filtering off the ether-insoluble bromide, is freed from uncombined bromine as described above, and the residue crystallised from petroleum ether. Any crystals separating out on cooling are filtered off, and their melting point is taken. By concentrating the filtrate, a further crop of tetrabromide may be obtained or even the second tetrabromide, melting at 56° C.

The filtrate from the last crop of crystals contains dibromide which can be isolated by evaporating off the solvent and weighing the residue. This is then best submitted to catalytic hydrogenation, whereby solid acids are obtained which can be readily examined. (Melting Point, mean molecular weight; cp. also Chap. XII.)

For the separation of oleic acid from other liquid fatty acids, *Farnsteiner* suggested a method based on the (comparative) insolubility of barium oleate in benzene containing alcohol, in which the barium salts of the less saturated acids are readily dissolved. Since the saturated acids behave like oleic acid, it would have been possible, provided the premises be correct, to separate a mixture of saturated and liquid acids of different unsaturation into a mixture of solid acids and oleic acid on the one hand, and of less saturated liquid acids on the other. *Lewkowitsch*,[1] however, has shown that this proposed method is of no use for quantitative purposes. Neither can the separation of oleic acid from less saturated fatty acids, by treating the mixed barium salts with moist ether, be effected with quantitative results.[2]

In some isolated cases the barium method is stated to have given satisfactory results for the separation of oleic acid from less saturated acids. In view of the conflicting evidence found in this respect in the recent literature on this subject, each individual case must be considered a problem of its own.

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[1] *Analyst*, 1900, 64; cp. also *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1903, vi. 161.

[2] Fahrion, *Zeits. f. angew. Chem.*, 1904, 1487.

A mixture of unsaturated acids cannot be resolved into its constituents by fractionating the methylesters (Chap. XII.), as the boiling points of the esters of the unsaturated acids lie so closely together that a separation by fractional distillation appears impossible. This is evidenced by the following table detailing the result of a fractional distillation of those methylesters of cotton seed oil fatty acids which boil above 200° C. under a pressure of 18 mm.

Fraction.	Boiling Point. °C.	Pressure. mm.	Quantity obtained from 535 Grams of Oil.	Iodine Value.
I.	up to 201·5	16 mm.	8 grams	77·13
II.	201·5-204	16 ,,	9 ,,	101·19
III.	204-207·5	16 ,,	20 ,,	123·51
IV.	207·5-210·5	16 ,,	83 ,,	130·87
V.	210·5-214·5	16 ,,	11 ,,	123·83
VI.	above 214·5	16 ,,	2 ,,	107·23
			133 ,,	

The identification of the several unsaturated acids by means of the weight of hydrogen they absorb—in other words, by their "*hydrogen value*"[1]—involves too complicated apparatus for a technical analysis, and furnishes no better results than does the determination of the much more expeditiously determined iodine value.

(Fokin[2] expresses the "hydrogen value" of a fatty substance by the number of cubic centimeters of hydrogen, calculated to 0° C. and 760 mm. pressure, absorbed by 1 grm. of substance.)

The same strictures hold good of the method of determining quantitatively the amount of *ozone* which the several unsaturated acids absorb (see Chap. III. p. 145).

9. Hydroxylated Fatty Acids

It has been shown above that hydroxystearic acid, as also dihydroxystearic acid, are sparingly soluble in cold petroleum ether. This behaviour to solvents would seem to suggest a method for the separation of hydroxylated fatty acids from the mixed fatty acids by treating the latter with petroleum ether. Experiments made by the author have, however, shown that such a method does not lead to useful results. Thus the mixed fatty acids from castor oil behave very much like castor oil itself (Vol. II. Chap. XIV.), that is, they dissolve in an *equal* volume of petroleum ether. A mixture of castor oil fatty acids with oleic acid, however, could not be separated by means of petroleum ether.

In case the nature of the hydroxylated fatty acid in a sample be known, its proportion in the mixed fatty acids may be obtained approximately by determining the increase in weight of the mixed fatty acids on boiling with acetic anhydride by *Lewkowitsch's* method. Let M be the molecular weight of the monohydroxylated acid, and i the increase of weight of A grams of the mixed fatty acids, then the percentage of hydroxylated acid y will be (cp. equation, p. 452).

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[1] Bedford, *Inaug. Dissert.*, Halle a/S, 1906.

[2] *Journ. Russ. Phys. Chem. Soc.*, 1908, 700.

$$y = \frac{100Mi}{A.42}.$$

In case the hydroxylated acid contain n hydroxyl groups, and consequently be able to assimilate n C_2H_2O groups, we shall find

$$y = \frac{100Mi}{A.n.42}.$$

This method will, however, only lead to useful results if the amount of hydroxylated acid present in the sample be large (as in the case of castor oil); otherwise the loss in weight caused through the formation of anhydrides of fatty acids may counterbalance any gain in weight.

In most cases it is therefore preferable to determine the *acetyl value of the mixed insoluble fatty acids* after freeing them from volatile acids by washing.

The washed fatty acids are acetylated in the manner described above, p. 428, and the acetylation product, after being washed free from acetic acid, is boiled with alcoholic potash in order to hydrolyse the anhydrides, and to saponify at the same time the acetylated acids with formation of potassium acetate and potassium soaps of the original fatty acids. On decomposing the solution with sulphuric acid, acetic acid is set free; this is then determined by the "distillation process" or by the "filtration process."

The acetyl value so obtained refers to the insoluble fatty acids and not to the oils and fats themselves. In some cases ("Blown Oils," Vol. III. Chap. XV.) it is advisable to determine the acetyl value of the original oil or fat, as well as that of its insoluble fatty acids. If both numbers are practically identical, the conclusion can be drawn that the acetyl value is due to the presence of a triglyceride of hydroxylated fatty acids. This happens in the case of castor oil.

Twitchell determines the "hydroxyl values" (see p. 430, footnotes) by esterification of the hydroxylated acid with fatty acid in the presence of *Twitchell's* reagent. For the details of this proposed method the reader must be referred to the original paper.[1]

For practical purposes the following table may be consulted:—

[TABLE

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[1] *Journ. Amer. Chem. Soc.*, 1907, 197; 566.

Acid.[1]	Formula.	Acetylated Acid.				Increase in Weight on Acetylating.
		Formula.	Molecular Weight.	Acetyl Value.	Saponification Value.	Per cent.
ydroxystearic .	$C_{18}H_{35}O_2(OH)$	$C_{18}H_{35}O_2(O . C_2H_3O)$	342	164·0	328·0	14·00
cinoleic . .	$C_{18}H_{33}O_2(OH)$	$C_{18}H_{33}O_2(O . C_2H_3O)$	340	165·0	330·0	14·09
hydroxystearic .	$C_{18}H_{34}O_2(OH)_2$	$C_{18}H_{34}O_2(O . C_2H_3O)_2$	400	280·5	420·75	26·58
ihydroxystearic .	$C_{18}H_{33}O_2(OH)_3$	$C_{18}H_{33}O_2(O . C_2H_3O)_3$	458	367·4	489·9	37·95
trahydroxystearic (Sativic)	$C_{18}H_{32}O_2(OH)_4$	$C_{18}H_{32}O_2(O . C_2H_3O)_4$	516	434·8	543·6	48·27
ntahydroxystearic .	$C_{18}H_{31}O_2(OH)_5$	$C_{18}H_{31}O_2(O . C_2H_3O)_5$	574	488·7	586·4	57·69
xahydroxystearic (Linusic)	$C_{18}H_{30}O_2(OH)_6$	$C_{18}H_{30}O_2(O . C_2H_3O)_6$	632	532·5	621·3	66·31

It should be noted that hydroxylated fatty acids are capable of forming (inner anhydrides, or) polymerisation products (cp. Chap. III. p. 114). The unsaturated hydroxylated acids (ricinoleic) are converted, by catalytic reduction in a current of hydrogen, into saturated hydroxylated acids, or at a somewhat higher temperature into saturated acids of the series $C_nH_{2n}O_2$.

Ricinoleic acid can be separated from other insoluble, non-hydroxylated fatty acids, in a direct manner, by making use of the insolubility of lead ricinoleate in low boiling petroleum ether (*Lane* [2]). Experiments made by the author [3] showed that by boiling the lead soap obtained from 5 grms. of castor oil with 50 c.c. of low boiling petroleum ether for one hour, and filtering the petroleum ether after cooling, 0·62 per cent (calculated on the oil) had been dissolved. On treating the undissolved lead soap with another 50 c.c. of petroleum ether for one hour, and filtering in the hot, 1·10 per cent were dissolved. On repeating the experiment with a fresh quantity of lead salt, 1·76 per cent were found to have been dissolved by hot petroleum ether.

For practical purposes the lead soap of ricinoleic acid may therefore be considered to be insoluble in cold petroleum ether.

10. "Oxidised" Fatty Acids

Under the term "oxidised" acids the author comprises [4] a class of fatty acids occurring in those oils and fats which have undergone a natural process of oxidation by exposure to the atmosphere,[5] such as highly rancid oils and fats, and especially "waste oils and fats" (see Vol. III. Chap. XVI.) or which have been artificially treated with oxidising agents, as in the process of blowing with air or oxygen [6] (see "Oxidised

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[1] For sabinic and juniperic acids see Chap. III. p. 211.

[2] *Journ. Soc. Chem. Ind.*, 1907, 597.

[3] Unpublished observations.

[4] Cp. *Analyst*, 1899, 323.

[5] Cp. G. Bouchard, *Les Matières Grasses*, 1912, 2779.

[6] Cp. French patent 368,543, and Swedish patent 15,802, 1902.

Oils," Vol. III. Chap. XV.). The change which some of the unsaturated acids undergo is not yet fully understood, but this much is certain, that through "blowing" or "oxidising," a certain proportion of acids are obtained which are characterised by their insolubility in petroleum ether.

The resinous substances which the author first observed in fatty acids obtained from liver and blubber oils (cp. Vol. II. Chap. XIV.) were found by *Tsujimoto* to be, most likely, oxidised acids derived from clupanodonic acid. Similar oxidised acids appear to be formed by the oxidation of highly unsaturated acids (arachidonic) in fatty acids from pigs' liver lecithins. They are not to be confounded with polymerised fatty acids, *e.g.* polymerised ricinoleic acid.[1] The "oxidised" fatty acids are soluble in alcohol, and, of course, in solutions of caustic alkalis; they are also slightly soluble in water. They are sparingly soluble in carbon bisulphide.

Fahrion,[2] who first proposed a method for the determination of "oxidised" acids in boiled linseed oil, assumed them to be hydroxylated acids, on account of their insolubility in petroleum ether, a property which characterises some well-known hydroxylated fatty acids. The fact, however, that the "oxidised" fatty acids can be separated from the other acids by petroleum ether, whereas (see p. 578) a mixture of castor oil fatty acids and oleic acid cannot be resolved into its constituents, proves that they form a special class of acids. Pending an inquiry into their nature, the author proposed for them the name "oxidised" acids.

The quantitative determination of oxidised acids in oils and fats is carried out as follows:[2]—4 to 5 grms. of the sample are saponified in the usual manner with alcoholic potash; the alcohol is evaporated off, the soap is dissolved in hot water, transferred to a separating funnel, and decomposed with hydrochloric acid. After cooling, the liquid is shaken with petroleum ether, boiling below 80° C., and allowed to stand until it has separated completely into two clear layers. The insoluble oxidised fatty acids will be found to adhere to the sides of the funnel or form a sediment in the petroleum ether layer. The aqueous layer is drawn off, the petroleum ether layer is poured off, if necessary through a filter, and the oxidised acids are washed with petroleum ether to remove adhering fatty acids. In case the amount of oxidised fatty acids be large, it is advisable to dissolve them in alkali, decompose the soap with hydrochloric acid, and shake out again with petroleum ether in order to remove completely any occluded soluble fatty acid. The oxidised acids are then dissolved in warm alcohol or ether, the alcoholic or ethereal solution is transferred to a tared basin, the alcohol or ether is evaporated off, and the residue dried until the weight remains constant. Thus the proportion of oxidised acids is found.

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[1] Fahrion (*Zeits. f. angew. Chem.*, 1909, 2093; 1910, 722, 1108) assumes that in the case of linseed oil "diperhydroxylinolenic" and "diperhydroxylinolic" are formed by oxidation, and that these hypothetical acids are converted subsequently into diketodihydroxylinolenic and ketodihydroxylinolic acids respectively. Reid's "superoxidised" linseed oil (see Vol. III. Chap. XV. "Linoleum") appears to belong to the same category of substances.

[2] *Zeits. f. angew. Chem.*, 1898, 782; 1903, 79; 1904, 1199; cp. also Kassner, *ibid.*, 1904, 1853.

In this manner the author prepared the oxidised acids from a number of blown oils and from solidified linseed oil (cp. Vol. III. Chap. XV. "Oxidised Oils"). The oxidised acids from a solidified linseed oil had the following characteristics: Neutralisation value, 168; saponification value, 199·2; apparent acetyl value, 130·2. Further information will be found under the headings of "Blown Oils" and "Boiled Oils." The following table [1] shows the manner in which the proportion of oxidised acids increases with the time of blowing:—

	Specific Gravity at 15·5° C.	Saponification Value.	Oxidised Acids. Per cent.
Oleic acid	0·8952	201·4	
Oleic acid, blown 2 hours at 120° C. . .	0·9098	204·9	0·62
,, ,, ,, 4 ,, 120° C. . .	0·9121	206·0	2·6
,, ,, ,, 6 ,, 120° C. . .	0·9123	208·3	3·5
,, ,, ,, 10 ,, 120° C. . .	0·9238	213·4	6·0

These oxidised acids exhibit considerable acetyl numbers (cp. Vol. III. Chap. XV.). The oxidised acids derived from marine animal oils—most likely derivatives of clupanodonic acid—are further oxidised by drying at 100° C. and then lose to some extent their ready solubility in alcohol (*Tsujimoto*).

Bouchard [2] isolated oxidised fatty acids from bone fat, linseed oil, arachis oil, sesamé oil, ravison oil, and cod liver oil. He also states that he obtained phenyl hydrazine compounds of the oxidised acids, without, however, giving details. For his speculative views as to the presence of carbonyl in hydroxylated groups the original paper must be consulted.

The following table, due to *Procter and Holmes*,[3] shows the changes in the specific gravity, refractive index, and iodine an Australian "oleine" underwent in blowing:—

Blown.	Specific Gravity.	Refractive Index.	Iodine Value.
Hrs.			
0	0·892	1·4620	88·0
3	0·892	1·4620	87·0
6	0·893	1·4620	84·0
9	0·894	1·4622	84·0
12	0·895	1·4623	82·0
15	0·895	1·4623	77·0
18	0·896	1·4624	74·0
21	0·897	1·4626	74·0
24	0·900	1·4628	73·0

---

[1] Cp. Lewkowitsch, *Laboratory Companion to Fats and Oils Industries*, Macmillan and Co., 1902, p. 76.

[2] *Les Matières Grasses*, 1912, 2779.

[3] *Journ. Soc. Chem. Ind.*, 1905, 1287.

Lewkowitsch[1] assumes in blown oils the presence of another kind of acid, differing from the " oxidised " acids. Pending further investigation they were termed **" unknown "** acids. Possibly the peroxidised acids described by *Fahrion*[2] belong to this group. Such acids also occur in soaps made from highly oxidised fatty acids and " waste " fats.

The investigation of the last two classes of fatty acids will be greatly facilitated by reducing the acids catalytically, when saturated acids would be obtained which can be more readily isolated and identified. According as the temperature in the catalytic reduction process is kept lower or higher hydroxylated saturated acids or saturated acids of the series $C_nH_{2n}O_2$ will be obtained.

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[1] *Analyst*, 1899, 323 ; 1902, 139.

[2] See footnote 1 p. 581.

CHAPTER IX

EXAMINATION OF UNSAPONIFIABLE MATTER

THE unsaponifiable matter is necessarily isolated as such in the course of its quantitative determination, and can therefore be further examined immediately.

In the case of natural oils and fats the quantity of unsaponifiable matter will, as a rule, be small, but in the case of waxes it constitutes a large proportion (about one-half) of the original substance, as pointed out already.

If the natural oils, fats, and waxes have been adulterated with such substances as paraffin wax, ceresin, mineral oils, neutral tar oils, and rosin oils, these substances will be obtained together with the naturally occurring unsaponifiable matter. Their detection and estimation will be considered briefly in this chapter.

The subject-matter of this chapter naturally divides itself into two groups: A,—Examination of those unsaponifiable substances which are naturally present in oils, fats, and waxes;

B,—Examination of foreign unsaponifiable substances that have been admixed with the substances considered under A.

A. EXAMINATION OF UNSAPONIFIABLE SUBSTANCES OCCURRING NATURALLY IN OILS, FATS, AND WAXES

1. Unsaponifiable Substances occurring in Oils and Fats

Considerable quantities of unsaponifiable substances in a natural oil or fat will betray their presence in the course of the process of saponification by a turbid solution, and when boiling is stopped they will be found floating on the top of the neutralised alcoholic soap solution as an oily layer. Small quantities, however, will always remain in solution, or form an emulsion with the soap solution.

The unsaponifiable matter in natural oils and fats consists in the main of cyclic alcohols, among which either cholesterol or sitosterol predominates, according as the oil or fat is of animal or vegetable origin. The latter alcohol is in some cases accompanied by stigmasterol, or brassicasterol. Of the alcohols of the ethane series hitherto only melissyl alcohol has been found in oils and fats.

The presence of hydrocarbons has hitherto been rarely recorded; recent observations (*e.g.* in the case of chrysalis oil, laurel oil, parsley seed oil, etc.) render it likely, however, that their presence may have been overlooked hitherto, as the total amount of unsaponifiable matter in most oils and fats is, as a rule, very small. The hydrocarbons, whenever their proportion in the unsaponifiable matter is considerable, can be separated from the alcohols by means of acetic anhydride, as described below (p. 601).

In addition to alcohols and hydrocarbons minute quantities of colouring substances, resinous substances, ethereal oils, and other foreign, perhaps also albuminoid, bodies occur. Some of the foreign substances possess optical activity and are characterised by absorbing considerable proportions of iodine. The examination of the unsaponifiable substances affords, therefore, a special problem in each given case. Hitherto such cases have been studied only exceptionally (see cotton seed oil, laurel oil, etc.); but a systematic investigation, such as has been undertaken by *Matthes* and his collaborators, may lead to important results by furnishing clues for the identification of those oils and fats the recognition of which in mixtures of oils and fats still causes difficulties (cp. Chap. XII.).

It will be convenient to subdivide the subject into—

A. *Examination of Alcohols.*
B. *Examination of Hydrocarbons.*

A. EXAMINATION OF ALCOHOLS

In this section the " Sterols " (Chap. III.) only will be dealt with, the discussion of the aliphatic alcohols and their separation from the cyclic alcohols being more appropriately deferred to the section describing the unsaponifiable substances occurring in " Waxes."

The detection of cholesterol and sitosterol (phytosterol), or a mixture of both, is of great importance whenever the question is placed before the analyst to decide whether a given sample is of animal or vegetable origin, or whether a mixture of vegetable and animal oils or fats is under examination (cp. Chap. XI.).

The method proposed by *Polenske*, to treat the crude unsaponifiable matter with low boiling petroleum ether in the cold, in which cholesterol and especially phytosterol are but sparingly soluble, does not always furnish useful results.[1] Thus *Matthes and Heintz*[2] observed that in the case of the crude unsaponifiable matter from Japan wax, phytosterol remained dissolved in the petroleum ether solution together with the oily portion of the unsaponifiable matter.

The colour reactions given above (Chap. III.) for cholesterol and sitosterol (phytosterol) are not distinct enough to allow of discrimination between the two alcohols. Recourse must, therefore, be had to the following methods :—

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[1] Cp. also Dunlop, *The Analyst*, 1907, 320.

[2] *Arch. d. Pharm.*, 1909 (247), 650.

(a) *Microscopic Examination* [1]

The unsaponifiable matter, after weighing, is dissolved in ether and poured into a small porcelain dish. The ether is allowed to evaporate off spontaneously, the mass is then dried on a water-bath, dissolved, after cooling, in the smallest possible quantity of absolute alcohol, and allowed to crystallise. Unless the amount of colouring matter and resinous substance present be large, well-defined crystals will be obtained. If foreign matters prevent the crystallisation of the alcohols, it is necessary to dissolve the unsaponifiable matter in 95 per cent alcohol and remove the colouring matters by treating in the hot with charcoal and filtering off the hot alcoholic solution.[2] (Instead of alcohol, petroleum ether may be used in conjunction with charcoal.) The filtrate is next evaporated to dryness, and again taken up with absolute alcohol. A few crystals are then taken out and examined carefully under the microscope. If either cholesterol or sitosterol (phytosterol) be present alone, the crystalline forms characteristic of cholesterol or sitosterol (phytosterol) will be found (Fig. 43).

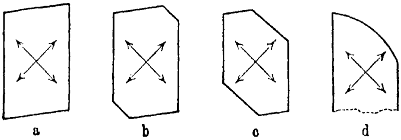

Fig. 43.—(*a*) Crystals of Cholesterol.

Crystals of cholesterol deposited from its hot alcoholic solution appear as a magma of laminæ, which are discerned, under the microscope, as very thin plates, often showing re-entering angles; these plates are apparently rhombic, but belong most likely to the triclinic system (*Bömer*). Sitosterol, on the other hand, crystallises in solid needles, grouped in tufts; under the microscope, long, solid needles are discerned, arranged in star or bunch-like groups; these crystals belong most likely to the monoclinic system.

If, however, a mixture of cholesterol and sitosterol (phytosterol) be present, the information furnished by the microscopic examination becomes very uncertain. According to *Bömer*, the components from a mixture of cholesterol and phytosterol do not crystallise separately; if the latter predominates, or is present in approximately the same proportion as cholesterol, the crystals cannot be distinguished from those of phytosterol, cp. Fig. 43 (*c*). If cholesterol predominates, needles of a quite different form separate (*Bömer*). Crystals obtained from (1) a mixture of 3 parts of sitosterol and 1 part of cholesterol melt at 135·6°-136·0° C.; (2) equal parts of sitosterol and cholesterol melt at 140·0°-141·5° C.; and (3) 1 part of phytosterol and 3 parts of cholesterol melt at 143·7°-145·0° C. The author, in his own experience, did not obtain the mixed forms of crystals from artificially prepared mixtures of cholesterol and phytosterol, but found that each constituent crystallised separately, the two different forms lying side by side in the mother liquor.[1] On crystallising rapidly, in most cases flocks showing distinct crystalline form separated; whenever crystals

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[1] Bömer, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1898, 544. The older term, "phytosterin test" or "phytosterol test," introduced by Salkowski in 1887, is not used in this work, in order to avoid confusion with the phytosteryl acetate test.

[2] If coprosterol (see Chap. III.) be the chief constituent of the unsaponifiable matter, as is the case in "Sewage Fats" (see Vol. III. Chap. XVI.), extraction with 80 per cent alcohol is best suited for the removal of impurities. Cholesterol and phytosterol are, however, very sparingly soluble in 80 per cent alcohol.

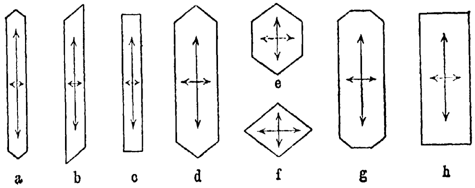

Fig. 43.—(*b*) Crystals of Phytosterol.

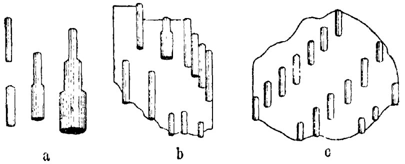

Fig. 43.—(*c*) Crystals from a mixture of Cholesterol and Phytosterol.

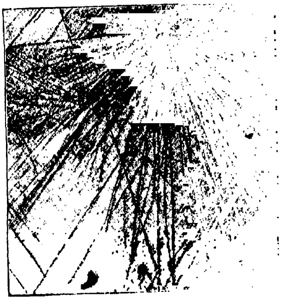
Fig. 44.—Crystals of Cholesterol (from alcohol).

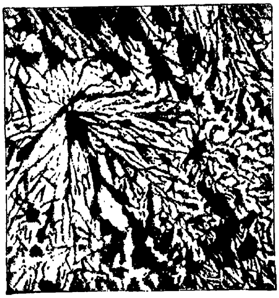
Fig. 45.—Crystals of Phytosterol (from ether).

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[1] *Journ. Soc. Chem. Ind.*, 1899, 557.

could be observed, they appeared to simulate the crystalline form of phytosterol. On filtering off the first crop of crystals and allowing them to crystallise again, better specimens were obtained, showing distinctly the individual forms of cholesterol side by side with the forms of phytosterol.

These observations are confirmed by *Zetsche*,[1] who published a number of drawings which are reproduced in Figs. 44 to 54.

The microscopic examination of the alcohols themselves should only be looked upon as a preliminary test, which does not permit a definite conclusion to be drawn as to the absence of cholesterol or phytosterol. More uncertain still become the microscopic indications if stigmasterol and brassicasterol are admixed with cholesterol and phytosterol.

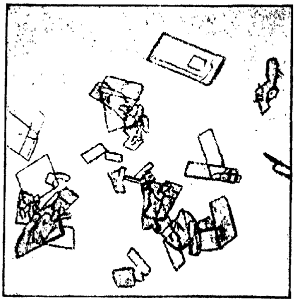

Fig. 46.—Crystals of Cholesterol (from alcohol; on glass cover).

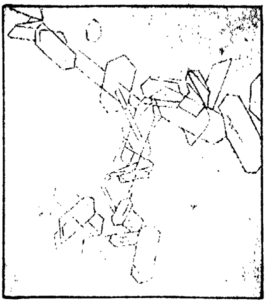

Fig. 47.—Crystals of Phytosterol (from alcohol; on glass cover).

In order to arrive at decisive results, it is necessary to carry out the "phytosteryl acetate test."

(*b*) *Phytosteryl Acetate Test*[2]

The alcoholic solution containing the crystals [see (*a*)] is brought to dryness on a water-bath, and the residue heated for a minute in a small porcelain dish with 2 to 3 c.c. of acetic anhydride per 100 grms. of original oil or fat over a small flame until the solution boils, the dish being kept covered with a watch-glass. The watch-glass is then removed, and the excess of acetic anhydride evaporated off on the water-bath. The contents of the dish are next heated with the smallest possible quantity of absolute alcohol; in order to prevent immediate solidification or crystallisation, a few c.c. of alcohol are added, and the mass is then allowed to crystallise. By spontaneous evaporation about one-half or one-third of the alcohol volatilises and the acetates crystallise out. The crystals are filtered off through a small filter, and washed with a little 95 per cent alcohol. The acetates are brought back from

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[1] *Pharm. Centralh.*, 1898, No. 49.

[2] Bömer, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1901; *ibid.*, 1902, 1018.

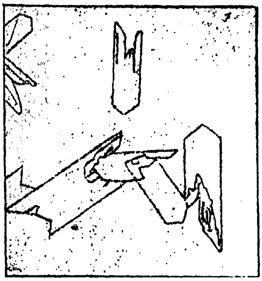

Fig. 48.—Crystals of Cholesterol containing 7 per cent of Phytosterol (from alcohol; on glass cover).

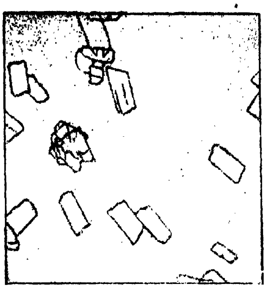

Fig. 49.—Crystals from Pure Lard (from alcohol; on glass cover).

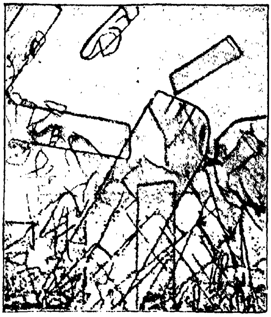

Fig. 50.—Crystals from Pure Lard (from alcohol; taken out of mother liquor).

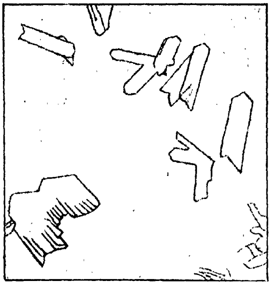

Fig. 51.—Crystals from Lard containing 5 per cent of cotton seed oil (from alcohol; on glass cover).

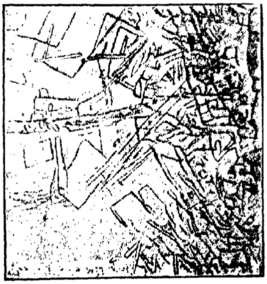

Fig. 52.—Crystals from Lard containing 5 per cent of cotton seed oil (from alcohol; on glass cover).

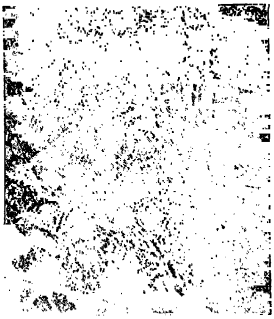

Fig. 53.—Crystals from Lard containing 5 per cent of cotton seed oil (from alcohol; taken out of mother liquor).

the filter into the dish, dissolved in 5 to 10 c.c. of absolute alcohol, and again allowed to crystallise. The crystals are filtered off, and their melting point is determined. Since cholesteryl acetate melts at 114·3°-114·8° C. (corr.), whereas crystals of phytosteryl acetate obtained from different oils and fats melt *above* 125° C., the melting point of the second crop of crystals will furnish preliminary information as to whether cholesterol only, or phytosterol only, is present. Ultimate reliance should not, however, be placed on the melting point of the second crop of crystals; for in most cases it is necessary to recrystallise the crystals at least three more times. If the melting point of the fifth or seventh crop of crystals be found to lie below 115° or 116° C., the absence of phytosterol can be pronounced with certainty. A gradual and distinct rise of the melting points, above 114° C., in the successive crystallisations is the best indication as to the procedure to be adopted. The following table, due to *Jäger*[1] and to *Klamroth*,[2] affords some guidance in practical cases :—

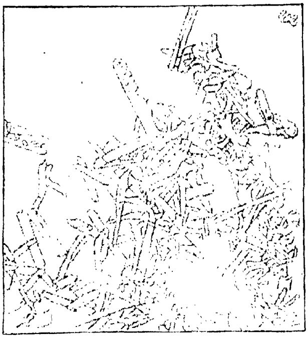

Fig. 54.—Crystals from Lard containing 10 per cent of cotton seed oil (from alcohol ; taken out of mother liquor).

Melting Points of Mixtures of Cholesteryl and Phytosteryl Acetates
(Jäger)

Cholesteryl Acetate of Melting Point 112·8° C.	Phytosteryl Acetate of Melting Point 129·2° C.	Melting Point of Mixture.
Per cent.	Per cent.	° C.
90	10	117
80	20	120·5
73·3	26·7	122·5
60	40	125
42·4	57·6	129
20	80	129·1
10	10	129·2

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[1] *Rec. d. trav. chim. Pays-Bas*, 1906 (25), 349.

[2] *Inaug. Dissert.*, Munich, 1911.

Melting Points of Mixtures of Cholesteryl and Sitosteryl Acetates

Cholesteryl Acetate.	Sitosteryl Acetate.	Jäger.	Klamroth.
Per cent.	Per cent.	° C.	° C.
100·0	..	113·6	113·0
96·0	4·0	115·0	114·2
86·4	13·6	119·1	118·0
79·5	20·5	121·3	120·6
66·6	33·4	125·0	124·2
50·0	50·0	127·1	127·0
38·3	61·7	128·2	127·8
33·3	66·7	128·3	128·2
26·4	73·6	128·3	128·0
15·5	84·5	128·2	128·0
10·1	89·9	128·1	127·8
0	100·0	127·1	127·0

In case the first crop of crystals be deeply coloured by foreign substances (a not infrequent occurrence), it is advisable to remove the bulk of the latter by pressing the crystals between filter paper before they are recrystallised.

The author has satisfied himself, by very exhaustive investigations carried out with a large number of oils and fats, as to the thorough reliability of this test. The experience thus gained constitutes one of the most important reasons for adopting in this work the subdivision of the natural oils and fats into those of vegetable and animal origin. A considerable number of other observers have also confirmed the reliability of this test; hence the opinion of a few chemists who found difficulties with this test may be disregarded as irrelevant.

A serious danger threatened the reliability of the phytosteryl acetate test by the practice of adding small quantities of paraffin wax to lard in order to mask the presence of vegetable oils and fats. *Polenske*[1] showed the influence which added paraffin wax has in this test, and gave a method not only for detecting and determining added paraffin wax quantitatively, but also for removing it, so that the phytosteryl acetate test can then be carried through without further difficulty. The correctness of *Polenske's* observations has been confirmed by *Lewkowitsch*,[2] who elaborated further methods for guarding against this possible circumvention of the phytosteryl acetate test.

In order to show how far the addition of paraffin wax may defeat the indications of the phytosteryl acetate test, *Polenske* experimented with 0·1 grm. of a mixture consisting of 94 per cent of cholesterol and 6 per cent of phytosterol, to which varying amounts of paraffin wax had been added. (The quantity of 0·1 grm. was chosen since 100 grms. of lard yield about 0·1 grm. of pure cholesterol.) This mixture of cholesterol and phytosterol gave in the phytosteryl acetate test the following numbers :—

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[1] *Arbeiten a. d. Kaiserl. Gesundheitsamte*, 1905, xxii. 576.

[2] *Chem. Revue*, 1907, 51.

Melting point of the 3rd crop of crystals	118° C.
„ „ „ 4th „ „	119° C.
„ „ „ 5th „ „	120° C.

The following table reproduces the results obtained with mixtures containing paraffin wax :—

Melting Points of Acetates obtained from 0·1 *Grm. of a Mixture of* 94 *per cent of Cholesterol and* 6 *per cent of Phytosterol, to which varying amounts of Paraffin Wax have been added.*

	Grms. of Paraffin Wax added.							
	0·002	0·003	0·005	0·007	0·01	0·02	0·05	0·1
	° C.	° C.	° C.	° C.	° C.	° C.	° C.	° C.
Melting points of the 3rd crop of crystals.	117·5	117·5	116·5	115	113	104	79	64
Melting points of the 4th crop of crystals.	118·5	118	117	112	108	89	60	55
Melting points of the 5th crop of crystals.	120	119·5	118	115	112	...	55	53

The amounts of paraffin wax added to the mixture of cholesterol and phytosterol are therefore, in the order of the vertical columns, 2 per cent, 3 per cent, 5 per cent, 7 per cent, 10 per cent, 20 per cent, 50 per cent, 100 per cent, or, calculated on the original fat, 0·002 per cent, 0·003 per cent, 0·005 per cent, 0·007 per cent, 0·010 per cent, 0·02 per cent, 0·05 per cent, 0·1 per cent. It will thus be seen that as little as 0·007 to 0·01 per cent of paraffin wax is capable of nullifying the indications of the phytosteryl acetate test ; smaller quantities are practically without any influence, whilst larger quantities are readily detected.

Polenske described a process for removing the paraffin wax, and, furthermore, a method for ascertaining its quantity. I have repeated *Polenske's* experiments, and can fully confirm their correctness.

In order to ascertain the influence of paraffin wax on pure cholesteryl acetate, I prepared mixtures of pure cholesteryl acetate, of the melting point 113°-113·5° C., and of paraffin wax, and determined their melting points.

Melting Point of Mixtures of Cholesteryl Acetate, Melting Point 113·5° *C., with Paraffin Wax* (*Lewkowitsch*)

	Melting Point.
97 per cent cholesteryl acetate+3 per cent paraffin wax	110° C.
93 „ „ „ +7 „ „ „	106° C.

On acetylating a mixture of 90 per cent of cholesterol and 10 per cent of paraffin wax, the presence of the latter can be detected at once by the appearance of a droplet of paraffin wax floating on the acetic anhydride solution. On subjecting the acetylated mass to recrystallisation, as is done in the phytosteryl acetate test, the following results were obtained :—

Melting point of the 2nd crystallisation . . .	90°-99° C.
„ „ „ 3rd „ . . .	90°-98° C.
„ „ „ 4th „ . . .	86°-89° C.
„ „ „ 5th „ . . .	86°-92° C.

It will thus be seen that the melting point falls rapidly, as must indeed be expected, since the paraffin wax, being insoluble in alcohol, separates in its entirety, together with a gradually diminishing amount of cholesteryl acetate.

As a corollary to these data, the result of experiments with 3 per cent of paraffin wax are given in the following table :—

Acetates from a Mixture of 97 *per cent of Cholesterol and* 3 *per cent of Paraffin Wax* (*Lewkowitsch*)

Melting point of the 1st crop of crystals . . .	104°-108° C.
„ „ „ 2nd „ „ . . .	104°-109° C.
„ „ „ 3rd „ „ . . .	103°-109° C.
„ „ „ 4th „ „ . . .	103°-109° C.
„ „ „ 5th „ „ . . .	103°-108° C.

The removal of the paraffin wax from the crude unsaponifiable matter is carried out according to *Polenske* by treating the unsaponifiable matter obtained from 100 grms. of fat [1] with 1 c.c. of petroleum ether (boiling below 50° C.) for twenty minutes in a water-bath at 15°-16° C., transferring the mass to a small funnel closed with cotton wool, and washing with five successive portions, each of one-half c.c. of petroleum ether. The paraffin wax is thus readily removed, whereas cholesterol and phytosterol, being much less soluble in cold petroleum ether, remain on the filter. The residue on the filter is then acetylated, and further treated as is usual in the phytosteryl acetate test. The drawback of this method is that a certain amount of the alcohols is washed away, but it offers the countervailing advantage that more cholesterol is removed than phytosterol, so that the indications of the phytosteryl acetate test become more distinct, the proportion of phytosterol (if any) to cholesterol being increased.

Polenske's method for the quantitative determination of paraffin wax consists in treating the unsaponifiable matter from 100 grms. of fat with 5 c.c. of concentrated sulphuric acid in a glycerin bath at 104° to 105° C. for one hour, when the alcohols are destroyed and the paraffin wax remains behind. The latter is extracted with low boiling petroleum ether, and weighed. In case minute quantities only of paraffin wax be present, the treatment with sulphuric acid should be repeated.

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[1] As caustic potash sticks obtained in commerce are not infrequently covered with paraffin wax, or have been cast in moulds coated with paraffin wax, this source of contamination with small quantities of paraffin wax must be guarded against when saponifying the fat. Cp. Bengen, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1910, xix. 271.

The following table, due to *Polenske*, shows the accuracy of the determination of paraffin wax in mixtures prepared from cholesterol and paraffin wax :—

	0·1 gr. of Cholesterol, to which had been added Paraffin Wax.					
	0·003 gr.	0·004 gr.	0·005 gr.	0·01 gr.	0·1 gr.	0 gr.
	Yielded Paraffin Wax.					
	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.
1. After 1st treatment with sulphuric acid .	0·0041	0·0056	0·0063	0·014	0·096	0·0029
2. After 2nd treatment with sulphuric acid .	0·0033	0·0041	0·0055	0·0105	0·092	0·0005

Unfortunately, by employing this method, the alcohols are destroyed, so that a confirmatory test cannot be carried out. From a somewhat extended experience of this test the author[1] has been led to adopt the following method: The unsaponifiable matter prepared from the suspected sample is converted into acetate in the usual manner. By observing the appearance of the acetic anhydride solution, paraffin wax amounting to 10 per cent of the alcohols can be detected at once by the appearance of a globule on the surface of the acetic anhydride solution. The globule of paraffin wax can be filtered off and, after washing with absolute alcohol, weighed. When determining the melting points of the consecutive crops of acetates the above given tables will serve as a guide. Only in case the presence of about 0·005 to 0·01 per cent of paraffin wax be suspected, further examination is required. In that event all the crystals and the mother liquors from the several crystallisations are united and boiled down to dryness. The mixture of acetates and of paraffin wax (if any) is saponified with alcoholic potash, and the soap solution extracted with ether, so as to recover the original unsaponifiable matter. If the work has been carried out with due care, the saponification value of the dried mass can be determined, as important information may thus be gained. This is brought out by the experiments detailed in the following table :—

Saponification Values of Mixtures of Cholesteryl Acetate and Paraffin Wax (*Lewkowitsch*)

	Calculated.	Found.
Cholesteryl acetate . . .	135·5	...
I. 0·1146 grm. cholesteryl acetate + 0·0100 grm. paraffin wax .	124·6	121·5
II. 0·1138 grm. cholesteryl acetate + 0·0200 grm. paraffin wax .	115·2	117·3

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[1] Lewkowitsch, *Chem. Revue*, 1907, No. 3.

The paraffin wax can then be determined quantitatively in the recovered unsaponifiable matter as directed above.

Windaus suggests purification of the "sterols" by means of digitonin (see Chap. III.), as follows:—

Dissolve the unsaponifiable matter in 50 parts of boiling 95 per cent alcohol (or in case there be present some insoluble matter prepare an extract by boiling out with alcohol) and add a hot 1 per cent solution of digitonin in 90 per cent alcohol until no longer a precipitate separates out. The precipitate settles out after a few hours' standing, is filtered on a Gooch crucible, washed with alcohol and ether, dried at 100° C., and weighed. From the equation

$$\underset{\text{(Digitonin-cholesterol.)}}{C_{82}H_{140}O_{29}} = \underset{\text{(Cholesterol.)}}{C_{27}H_{46}O} + \underset{\text{Digitonin.}}{C_{55}H_{94}O_{28}}$$

it follows that if a be the quantity of digitonincholesterol found, the quantity of sterol s is obtained by multiplying a with 0·2431 $\left(\frac{386\cdot35}{1589}\right)$. For practical purposes the factor 0·25 is sufficiently accurate.

In the author's experience the digitonin method does not always yield satisfactory results.[1]

The phytosterol referred to in the preceding lines should not be taken as consisting of a chemical individual. Since *Windaus and Hauth*[2] have found that the "phytosterol" of Calabar beans consists of a mixture of true phytosterol (sitosterol) and stigmasterol, the presence of the latter—conjointly with that of phytosterol—in vegetable oils has been proved in the case of rape oil, soya bean oil, etc.

The separation of stigmasterol from phytosterol is effected by acetylating the mixed alcohols and brominating their acetates, when tetrabromostigmasteryl acetate and dibromophytosteryl acetate are formed. The separation of the two esters is easily effected, as tetrabromostigmasteryl acetate is insoluble in a mixture of glacial acetic acid and ether, whereas dibromophytosteryl acetate is soluble. The original alcohols are then regenerated from their bromoderivatives by reducing with zinc dust and acetic acid in alcoholic solution. From the recovered acetates the original alcohols are prepared, and identified by their melting points, etc.

In a similar manner brassicasterol is separated from phytosterol.

For the separation of cholesterol from phytosterol the following method, based on the behaviour of their respective dibromides (see Chap. III. pp. 267, 276) to a mixture of ether and glacial acetic acid, was proposed by *Windaus*.[3] The *modus operandi* is best illustrated by an example given by *Windaus*:—A mixture of 4 grms. of phytosterol and 0·4 grm. of cholesterol was dissolved in 44 c.c. of ether, and 44 c.c. of a solution of 5 grms. of bromine in 100 c.c. of glacial acetic acid was added. No crystals of cholesterol dibromide separated. On adding 11 c.c. of 50 per cent acetic acid a precipitate weighing 0·14 grm. and consisting of practically pure cholesterol dibromide was obtained. This precipitate was washed with 22 c.c. of glacial acetic acid and subsequently with 11 c.c. of 50 per cent acetic acid. On adding the wash liquors to the main filtrate a further precipitate weighing 0·24 grm. was obtained, which consisted of a mixture of cholesterol and phytosterol dibromides. From the filtrate 3 grms. of phytosteryl acetate could be recovered. *Holde*[1] stated that this method is unreliable when only small quantities of cholesterol are contained in the mixed alcohols. The author,[2] however, obtained satisfactory results by *Windaus'* method in the case of mixtures of animal oils and fats with vegetable oils and fats containing at least 20 per cent of the former. With smaller quantities of animal oils and fats the results were no longer accurate enough to permit of quantitative interpretation. For such cases the author suggests the preliminary partial separation of the mixed alcohols by means of petroleum ether, in which cholesterol is much more soluble than phytosterol (Chap. III. p. 266 and p. 276). The ethereal solutions are evaporated to dryness and treated once more with petroleum ether. The alcohols obtained on evaporation are then treated by one of the two preceding processes.

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[1] Cp. Chap. III. p. 264. Cp. also H. Matthes and A. Dahle, *Archiv d. Pharm.* 1911 (249), 442.

[2] *Berichte*, 1906, 4381; 1907, 3681.

[3] *Chem. Zeit.*, 1906, 1011.

The bromide method can be used as a check on the phytosteryl acetate methods as regards quantitative interpretation.

If the crude unsaponifiable matter be very impure, the purification by means of the digitonin product may be interpolated as a preliminary operation.

Klamroth[3] studied the application of the bromo-thermal test to the quantitative determination of mixtures of cholesterol, phytosterol, and stigmasterol. The numbers given in the following tables show that the "Heat of Bromination" test affords a very convenient and even accurate method.

Bromo-thermal Test of "Sterols" and their Acetates

Sterol.	° C. after two Minutes.
Cholesterol	7·38
Sitosterol	7·00
Stigmasterol	14·3

Acetate.	Heat of Bromination. ° C.	
	Found after 2 min.	Calculated from iodine value.
Cholesterylacetate . . .	4·0	6·79
Sitosterylacetate	6·5	6·79
Stigmasterylacetate . . .	12·7	12·42

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[1] *Zeits. f. angew. Chem.*, 1906, 1609; cp. also P. Werner, *Inaug. Dissert.*, Berlin 1911, and Chap. III. p. 267.

[2] *Jahrbuch der Chem.*, 1906, xvi. 406.

[3] *Inaug. Dissert.*, Munich, 1911.

Mixtures of Cholesteryl- and Sitosterylacetate

Mixture containing		Heat of Bromination. °C.		Calculated from Heat of Bromination.	
Cholesteryl-acetate.	Sitosteryl-acetate.	Found.	Calculated.	Cholesteryl-acetate.	Sitosteryl-acetate.
Per cent.	Per cent.			Per cent.	Per cent.
90	10	4·3	4·35	88	12
50	50	5·3	5·35	48	52
20	80	5·95	6·0	22	73
10	90	6·3	6·25	8	93

Mixtures of Cholesteryl- and Stigmasterylacetate

Mixture containing		Heat of Bromination. °C.		Calculated from Heat of Bromination.	
Cholesteryl-acetate.	Stigmasteryl-acetate.	Found.	Calculated.	Cholesteryl-acetate.	Stigmasteryl-acetate.
Per cent.	Per cent.			Per cent.	Per cent.
95	5	4·4	4·43	95·5	4·5
55	45	8·1	8·0	54·0	46·0
50	50	8·2	8·35	52·0	48·0
80	20	11·0	11·0	80	20·0

Mixtures of Sitosteryl- and Stigmasterylacetate

Mixture containing		Heat of Bromination. °C.		Calculated from Heat of Bromination.	
Sitosteryl-acetate.	Stigmasteryl-acetate.	Found.	Calculated.	Sitosteryl-acetate.	Stigmasteryl-acetate.
Per cent.	Per cent.			Per cent.	Per cent.
95	5	6·75	6·81	96·0	4·0
50	50	9·7	9·6	48	52·0
20	80	11·5	11·40	20	80·0

Comparative tables showing the relation between heat of bromination and melting point of cholesteryl- and sitosterylacetate, cholesteryl- and stigmasterylacetate, sitosteryl- and stigmasterylacetate respectively, are given below :—

[TABLE

Mixtures of Cholesteryl- and Sitosterylacetate

Heat of Bromination.	Melting Point.	Cholesterylacetate.	Sitosterylacetate.
°C	°C.	Per cent.	Per cent.
4	113·0	100·0	0
4·2	117·6	92·0	8·0
4·35	118·6	86·0	14·0
4·5	120·5	80·0	20·0
4·7	123·2	72·0	28·0
5·05	126·2	58·0	42·0
5·4	127·5	44·0	56·0
5·6	128·4	36·0	64·0
5·9	128·2	24·0	76·0
6·15	128·0	14·0	86·0
6·5	127·0	0	100·0

Mixtures of Cholesteryl- and Stigmasterylacetate

Heat of Bromination.	Melting Point.	Cholesterylacetate.	Stigmasterylacetate.
°C	°C.	Per cent.	Per cent.
4	113·0	100·0	0
5·4	117·8	84·0	16·0
5·9	119·2	79·0	21·0
6·1	120·4	76·0	24·0
7·05	123·0	65·0	35·0
10·3	133·0	28·0	72·0
11·4	137·0	15·0	85·0
12·7	141·0	0	100·0

Mixtures of Sitosteryl- and Stigmasterylacetate

Heat of Bromination.	Melting Point.	Sitosterylacetate.	Stigmasterylacetate.
°C.	°C.	Per cent.	Per cent.
6·5	127·0	100·0	0·0
7·0	128·2	92	8
7·5	130·4	84	16
8·15	132·8	73	27
8·55	133·6	67	33
8·9	134·5	61	39
9·2	135·0	56	44
10·0	136·0	44	56
11·4	139·0	21	79
12·7	141·0	0	100

Instructive is also the following table, in which the heat of bromination and melting point are given of successive crystallisations from alcohol of a mixture of 80 parts of cholesterylacetate and 20 parts of acetates of Calabar bean phytosterols. The Calabar bean phytosterols were chosen for comparison, inasmuch as they represent a typical and presumably constant mixture of sitosterol and stigmasterol.

Fraction.	Heat of Bromination.	Melting Point.
	° C.	° C.
1.	5·1	120·0
2.	5·35	122·0
3.	5·7	126·4
4.	6·4	128·2
5.	7·3	130·4

Polenske[1] observed that from old and rancid fat there were always obtained larger quantities of unsaponifiable matter than from fresh fat. In the case of old rancid fat it was not possible to obtain even by repeated crystallisation pure alcohols of normal melting points. The melting points of the acetates obtained from those alcohols are also lower than those derived from the corresponding fresh fats.

B. EXAMINATION OF HYDROCARBONS

The isolation of hydrocarbons contained in the unsaponifiable matter from oils and fats, their separation from the sterols and purification of the hydrocarbons themselves, involves a complicated investigation which hardly falls within the province of a technical examination. In order to prepare sufficient quantities of hydrocarbons, it is necessary to work with very considerable quantities of oils and fats.

It must, therefore, suffice here to enumerate those hydrocarbons which have been isolated hitherto in a state of purity, and to refer for the special methods adopted for this purpose to the original papers, given in Vol. II. under the headings of the oils and fats, from which the hydrocarbons have been derived :—

Hydrocarbons Isolated from Oil and Fats

	Occurrence in	Melting Point.	Observer.
		° C.	
$C_{20}H_{42}$, Petrosilane .	Parsley seed oil	69	Matthes and Heintz
$C_{28}H_{58}$	Chrysalis oil	62·5	Menozzi and Moreschi
$C_{20}H_{42}$, Laurane. .	Laurel oil	69	Matthes and Sander
$C_{31}H_{64}$	Kosam seed oil	67-68	Power and Lees
$C_{30}H_{48}$ (Amyrilene ?)	Cacao butter	...	Matthes and Rohdich
(?)	Buck thorn oil	81-82	Krassowski

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[1] *Arbeiten aus dem kaiserl. Gesundheitsamte*, 1912, 38, Heft 5.

2. Unsaponifiable Substances occurring in Waxes

In order to effect complete hydrolysis of the esters in waxes, it is advisable to saponify with double normal alcoholic potash under pressure, or preferably with sodium alcoholate (cp. Chap. II.).

The unsaponifiable constituents of waxes consist of aliphatic alcohols [cetyl alcohol, ceryl alcohol, melissyl (myricyl) alcohol, etc.], or a mixture of these with sterols ("phytosterol" in the case of vegetable waxes and cholesterol and isocholesterol in the case of wool wax); in the case of some solid waxes considerable proportions of hydrocarbons are also found. Since the unsaponifiable matter does not consist of one single chemical individual, *ultimate analysis* does not furnish any useful data. Nor will the determination of the *melting point* yield more than some slight preliminary information, as will be seen from the following table giving the melting points of those substances which are most likely to be met with in the unsaponifiable matter of solid waxes:—

Unsaponifiable Substances.	Melting Point, ° C.
Cetyl alcohol	50
Ceryl alcohol	79
Melissyl (myricyl) alcohol . .	85
Cholesterol	148·4-150·8
Isocholesterol	137-138
Beeswax hydrocarbon $C_{27}H_{56}$ . .	60·5
,, ,, $C_{31}H_{64}$ . .	67

With regard to the alcohols occurring in liquid waxes, cp. Vol. II. Chap. XIV. "Sperm Oil."

If a mixture of several of these substances be present, the indications furnished by the melting point become of still less importance, as small quantities of impurities considerably depress the melting point. Only in case a very high melting point has been obtained, conclusions may be drawn as to the presence of cholesterol, but it should be remembered that a mixture of cholesterol and isocholesterol melts below 100° C.

Ultimate analysis and the determination of the melting point will only furnish decisive information, if in the course of a detailed examination pure substances have been obtained.

For the purposes of technical analysis the following two processes will furnish guidance as to the methods to be adopted for further investigation.

1. Weigh off accurately from 3 to 5 grms. of the mixed unsaponifiable substances and boil with twice the weight of acetic anhydride in a flask under a reflux condenser. Pour the acetylated mass into 300 c.c. of boiling water so as to hydrolyse the excess of acetic anhydride, allow to cool, and then filter the separated mass through a weighed filter (cp. Chap. VI. "Mono- and Di-glycerides"), wash until the wash waters are no longer acid, and dry to constant weight (*Lewkowitsch*).

From the increase in weight, preliminary information may be gathered as to the proportion of alcohols present. For this purpose the last column of the table given p. 604 should be consulted.

2. Boil the unsaponifiable substance with acetic anhydride, as described under 1, and observe the appearance of the hot liquid. The following three cases may present themselves :—

(*a*) The unsaponifiable matter is completely dissolved in acetic anhydride, and no separation takes place on cooling. This indicates that *aliphatic* alcohols are present.

(*b*) The unsaponifiable matter is completely dissolved in the hot liquid, but on cooling a magma of crystals separates out. This indicates the presence of *cholesterol* (isocholesterol) or *phytosterol*, or of some higher aliphatic alcohols, or of a mixture of these substances.

(*c*) The hot solution is not homogeneous, a clear oily layer floating on the top of the hot acetic anhydride solution. This indicates the presence of notable quantities of hydrocarbons (naturally occurring hydrocarbons, or admixed paraffin wax, ceresin, etc.). Any alcohols such as described under (*a*) and (*b*) would remain dissolved in the hot acetic anhydride. The presence of cholesterol or (and) phytosterol would be recognised as under (*b*). If the lower layer be clear on cooling, alcohols of the aliphatic series may be present.

An approximate separation of hydrocarbons from the alcohols can be effected by the following method, which the author has frequently employed with advantage :—The hot acetylated mass is transferred to a small separating funnel of thin-walled glass, as little acetic anhydride as possible being used to rinse the flask. The separating funnel is carefully warmed, so that all the alcohols remain in solution and two distinct layers are obtained. If too much acetic anhydride be used, notable quantities of hydrocarbons pass into solution.[1] The clear lower layer is drawn off whilst hot, and examined for the presence of alcohols, as described below; the upper layer of hydrocarbons is washed with a small quantity of acetic anhydride in the hot.

The hydrocarbons are then allowed to cool, rinsed with boiling water on to a filter, and weighed. They may then be further examined by determining their melting point and iodine absorption, and if deemed necessary purified by re-crystallisation from suitable solvents and subjected to elementary analysis. The hot acetic anhydride solution containing the alcohols is run into boiling water, and the separated acetates (of aliphatic alcohols, cholesterol, etc.) are washed on a filter until the wash-waters are no longer acid.

By determining the saponification value of the acetates on the filter in the manner described under the heading "Saponification Value" (Chap. VI.), and comparing the numbers so found with those recorded in the table given below, some further information will be gathered as to the composition of the original alcohols.

If a mixture of aliphatic alcohols with cholesterol or isocholesterol be suspected, it will be useful to remember that the acetates of the sterols require larger quantities of hot 95 per cent alcohol for complete solution than do the aliphatic alcohols. Thus a separation of cholesteryl and isocholesteryl acetates from the acetates of the aliphatic alcohols can be attained to some extent. Complete separation, however, cannot be effected, as has been shown by *Lewkowitsch*.[1] From a mixture prepared from weighed quantities of cholesterol and cetylalcohol he obtained in two experiments 60 and 69 per cent of the theoretical quantities of pure cholesteryl acetate in the first crop of crystals, whilst the second crop of crystals—9 per cent—contained notable quantities of cetyl acetate. Again, on boiling wool wax alcohols [consisting of cholesterol, isocholesterol, ceryl alcohol, and other unknown alcohols] with acetic anhydride, and trying to separate the acetates by crystallisation from alcohol, *Lewkowitsch* isolated ceryl acetate in a crystalline state, whilst the acetates of the cholesterols, with the acetates of the unknown alcohols, formed oily substances from which no crystals could be obtained.

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[1] Cp. Marcusson, *Mitth. König. Tech. Vers.-Anst.*, 1900, 261; Dunlop, *Journ. Soc. Chem. Ind.*, 1908, 63.

If cholesterol and isocholesterol be absent and only aliphatic alcohols are present (as in the case of carnaüba wax, beeswax, spermaceti, and insect wax) the mixed acetates may be approximately resolved into their constituents by fractional crystallisation from alcohol. The determination of the saponification values and also of the iodine values will furnish important clues. For further examination the acetates are converted into the corresponding free alcohols by saponification with alcoholic potash. Incidentally the determination of the saponification values is combined with this operation; when the excess of alcoholic potash is titrated back, the alcohols separate out. These are precipitated completely by addition of water, and can be recovered quantitatively for further examination. It will be useful to determine the melting point and the iodine value of the isolated alcohols, and to examine them qualitatively for cholesterol and isocholesterol.

A. Leys[2] proposes a method for the separation of alcohols from hydrocarbons (especially in the case of beeswax and carnaüba wax), based on the treatment of the mixture with an amyl-alcoholic solution of fuming hydrochloric acid (equal parts) in the hot; the alcohols are thereby dissolved, whereas the hydrocarbons separate out as an insoluble mass. *Leys* saponifies 10 grms. of the substance with 25 c.c. of alcoholic potash (45 grms. potash in 1000 c.c. of absolute alcohol and 50 c.c. of benzene in a special flask[3] (see Fig. 55)). When the saponification is completed, 50 c.c. of hot water are added and boiling continued under a reflux condenser for a few minutes. The soap solution is drawn off while hot, and the benzene solution is washed with hot water. After withdrawing the wash-water completely, the benzene solution is evaporated to dryness in a porcelain dish. The residue is then transferred with 100 c.c. of hot amyl alcohol to a beaker and an equal volume of fuming hydrochloric acid is added. This is then boiled over an asbestos plate; the alcohols dissolve, whereas the hydrocarbons separate on the top as a cake. The hydrocarbons are taken off and boiled out once more with a mixture of 25 c.c. of amyl alcohol and 25 c.c. of fuming hydrochloric acid. After cooling, the cake of hydrocarbons is taken off, rinsed with water, dried, and weighed. The alcohols remaining in the lower layers are boiled with water, the acid solution is drawn off and the amyl alcohol solution well washed. The amyl alcohol is finally distilled off, the residue dissolved in benzene, and after evaporating the latter, are weighed. The alcohols may be further examined by the methods described below.

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[1] *Journ. Soc. Chem. Ind.*, 1892, 143.

[2] *Journal de l'Pharm. et de Chimie*, 1912 (v.), 577.

[3] Obtainable from J. Thurneyssen, 58 rue Monsieur le Prince, Paris.

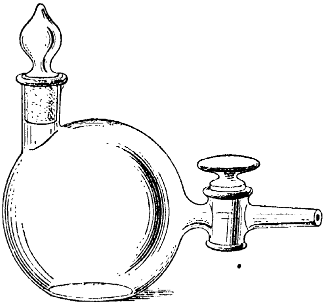

Fig. 55.

Cholesterol and isocholesterol can to some extent be separated from one another by means of their benzoates. These are prepared by heating the alcohols with 4 parts of benzoic anhydride[1] in a sealed tube to 200° C. for thirty hours (p. 271). The product is boiled out repeatedly with alcohol, in order to remove any adhering aliphatic alcohols. The mixed benzoates are then dissolved in ether and allowed to crystallise. Cholesteryl benzoate crystallises in hard rectangular plates, whereas isocholesteryl benzoate is obtained as a light crystalline powder, which can be roughly separated from the former by decantation and elutriation. Cholesteryl benzoate melts at 150°-151° C., isocholesteryl benzoate at 190°-191° C. For a confirmatory test, the benzoates should be saponified with alcoholic potash, and the cholesterol and isocholesterol precipitated by diluting with water. The separated alcohols may be further identified by their optical rotations and their melting points.[2]

In the following table will be found a synopsis of those characteristics which prove of assistance in the examination of the solid unsaponifiable substances:—

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[1] Schulze, *Berichte*, 5. 1076; 6. 251, 571; *Journ. f. prakt. Chem.* 115. 163.

[2] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 142. For a method of ascertaining the composition of an aliphatic alcohol by converting it into its palmitate and distilling the latter, when the corresponding unsaturated hydrocarbon is obtained, see F. Krafft, *Berichte*, 1883, 3018.

[TABLE

According to *Hell*, the substance, intimately mixed with soda-lime, is introduced into the tube *i* (Fig. 56), and the mixture covered with soda-lime. In order to reduce the volume of air to the smallest possible amount, the sealed tube *k* is placed inside tube *i*. The latter is closed by a perforated india-rubber stopper *p* provided with tube *r*, which connects *i* with a *Hofmann* gas burette, filled completely with mercury, and closed at the top by means of the three-way tap *h*. The tube *i* is then immersed in an air-bath provided with a thermometer. Tube *i* is at first brought into communication with the air by tap *h*, then the height of the barometer and temperature of the air is noted and *i* connected with the burette by suitably turning the three-way tap. Part of the mercury is then withdrawn by tap *q*, and the air-bath heated to 300°-310° C., until the level of the mercury remains constant. The apparatus is then allowed to cool down to the temperature of the room, when the original pressure is again established by adding mercury. The volume of gas is then read off and calculated to 760 mm. pressure and 0° C. The hydrogen may be measured either after drying the gas, or after saturation with moisture, when a correction for the tension of the water vapour must be made. The drying of the gas is done most conveniently by taking a longer tube *i*, and placing over *k* a layer of strongly heated soda-lime.

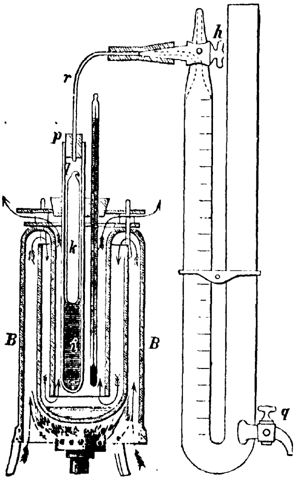

Fig. 56.

A. and P. Buisine[1] showed that the reaction does not take place quantitatively if a wax be heated directly with *potash-lime* (1 part of caustic potash and 2 parts of lime). They proceed therefore in the following way: 2 to 10 grms. of a wax, weighed accurately, are melted in a porcelain crucible, and an equal weight of finely powdered caustic potash is stirred into the melted mass. The hard mass obtained on cooling is carefully powdered and intimately mixed with three parts of potash-lime for every part of wax weighed off. The mixture is placed in a test-tube or a pear-shaped flask, care being taken that the vessel is nearly filled; the mass is put into an iron still, filled with mercury, and closed by a cover having three nozzles. Through one of these passes the outlet tube from the glass vessel containing the substance, whilst into the second is fixed a thermometer; the third nozzle is provided with a long iron tube to condense or lead away the mercury vapours.

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[1] *Monit. scientif.*, 1890, 1127.

Instead of collecting the gas in a *Hofmann* burette, *A. and P. Buisine* prefer the apparatus designed by *Dupré,* and shown in Fig. 57. The gas evolved can be made to enter the vessel E either from the top, by opening tap A, or from the bottom, by opening tap B. The internal diameter of the glass tubes provided with its taps A and B is small. When all connections have been made, bottle E is filled with water by raising bottle F until water enters C. Tap D is then closed, bottle F lowered, tap A opened, and the mercury heated. At 180° C. the reaction commences; the temperature is, however, raised to 250° C. and kept thereat for two hours. If gas is liberated copiously, tap A is closed and B opened; thus it is easy to control the progress of the reaction. When bubbles of gas no longer rise through the water, tap B is closed and A opened. The apparatus is then allowed to cool down, and the gas introduced into the eudiometer; the volume read off is reduced to 760 mm. pressure and 0° C. and calculated to 1 grm. of substance. With the aid of the above-given table the number of c.c. of hydrogen found is calculated to the proportion of the alcohol assumed to be present. It is of course obvious that simpler apparatus than the one shown in Fig. 57 may be readily constructed. For the modification employed by *Ahrens and Hett* cp. Vol. II. Chap. XIV. "Beeswax."

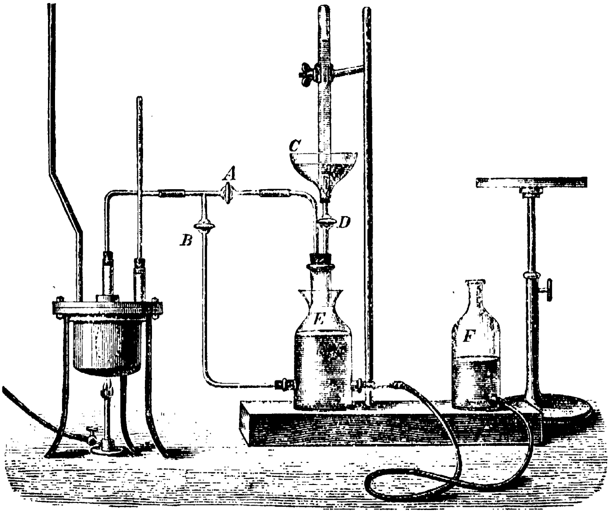

Fig. 57.

If oleic acid be present the temperature should not be allowed to exceed 250° C., as otherwise palmitic acid is formed with evolution of hydrogen (see Chap. III. p. 158).

Since cholesterol remains practically unchanged, it can be separated off by extracting the powdered residue with ether in a *Soxhlet* extractor. Any solid hydrocarbons, which have not been removed beforehand (by the acetic anhydride method, p. 601), will be extracted simultaneously with the cholesterol, and can now be separated from it by means of acetic anhydride.

The soda-lime residue, freed from cholesterol and hydrocarbons, contains the salts of the fatty acids corresponding to the alcohols present. Thus cetyl alcohol, ceryl alcohol, and melissyl alcohol yield, respectively, palmitic acid, cerotic acid, and melissic acid. The salts are decomposed by means of sulphuric acid, and the liberated fatty acids collected, examined, and identified by their melting points and mean molecular weights. If a mixture of all three acids be present, palmitic can be readily separated from the other two by converting the mixed acids into sodium soaps and treating the mixture with 40 per cent alcohol, when sodium cerotate and melissate remain undissolved and can be filtered off (cp. Chapter XI.). The soaps are then decomposed by adding mineral acid and the mixture of cerotic and melissic acids is examined for melting point and mean molecular weight. If the melting point warrants the assumption that only cerotic and melissic acids are present, the respective proportions of cerotic and melissic acids can be calculated *approximately* from the mean molecular weight of the mixture (see Chapter XI.). With regard to the unsaponifiable matter in " montanwax " see Vol. III. " Montanwax."

B. DETECTION AND DETERMINATION OF ADMIXED UNSAPONIFIABLE SUBSTANCES

Admixed *solid* unsaponifiable substances, such as paraffin wax and ceresin, are detected and determined as described above.

In manufactured products, such as " commercial stearine," " Turkey red oil," etc., lactones or anhydrides occur which may be mistaken for unsaponifiable matter. Due care must therefore be taken in such cases to guard against error (cp. " Lactones," Chapter VIII. p. 520). It should also be remembered that waxes are saponified with difficulty ; any portions that may have escaped saponification would be found amongst the unsaponifiable matter.

Considerable quantities of *liquid* unsaponifiable substances may be due to legitimate admixture with hydrocarbons, as in the case of burning or lubricating oils (cp. Vol. III. Chap. XV.). In the majority of instances, however, they constitute adulterants.

Liquid unsaponifiable substances may consist of mineral oils, rosin oils, or tar oils, or a mixture thereof. In case only one class of these oils be present, the specific gravity will furnish the readiest means of identifying the liquid unsaponifiable matter, as may be gathered from the following table :—

Class of Oil.	Specific Gravity.
Heavy mineral oils	. 0·840-0·990
Rosin oils	. 0·960-1·01
Coal tar oils	higher than 1·01

Mineral Oils.—The lower limit of their specific gravity has been placed here by the author at 0·840, since admixture with mineral oils of lower specific gravity is as a rule not practised, as the specific gravity alone (as also the low flash point) of an adulterated fatty oil would reveal the presence of hydrocarbon oils of lower gravity. If mineral oils be present, the distillation products of crude petroleum, shale, and lignite, boiling at 250°-300° C. and having the specific gravity 0·855-0·900, may be expected. Sometimes also higher boiling oils of the specific gravity 0·900-0·930 are met with in adulterated oils and fats.

Mineral oils of still higher specific gravity, up to 0·990 (Texas oils), are mostly too dark to be used for admixture with oils and fats. Fractions boiling below 250° C., such as those contained in "kerosene" (burning oil), will only be found in very small quantities; they are best detected by the flash point test (see Vol. III. Chap. XV.).

Rosin Oils.—The specific gravity of these oils which are obtained by subjecting colophony (rosin) to destructive distillation (cp. Chap. X. p. 617) and fractionating the distillate into "rosin spirit" ("pinolin") and "rosin oil," ranges as a rule from 0·96 to 0·99; yet rosin oils having the specific gravity 1·01 are also met with in commerce. The chemical composition of rosin oils is not yet fully understood; they consist mostly of hydrocarbons related to the terpenes, but contain also, according to the care exercised in distilling, larger or smaller quantities of "*rosin* acids" and other oxygenated substances. This is shown in the third column of the following table, in which the analyses of a number of commercial rosin oils,[1] carried out in the author's laboratory, are detailed:—

Commercial Rosin Oils (Lewkowitsch)

Rosin Oil.	Specific Gravity at 60° F.	Rosin Acids, calculated to Combining Weight 316.[2]
		Per cent.
"Soft"	0·9878	9·2
"Medium" . . .	0·9946	26·3
"Hard" . . .	0·9974	31·2
"	0·9877	19·6
"	0·9890	20·3
"	0·9982	18·6
"Siccative" . . .	0·9955	4·9
"Extra hard oil" . .	1·0115	18·4

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[1] With regard to rosin oil from *Pinus longifolia* cp. F. Rabak, *Pharm. Review*, 1905 (23), 229.

[2] It is doubtful whether the "rosin acids" are actually "abietic acid," as has been assumed for purposes of calculation, or rather acidic products due to the destructive distillation of abietic acid (cp. F. Schulz, *Chem. Revue*, 1909, 187).

It should be noted that any rosin oils found in the unsaponifiable matter are free from the rosin acids originally contained in the commercial oils, the rosin acids having combined with caustic potash to form soap in the saponification process. Therefore, if rosin oil has been detected, the original amount of admixed "rosin oil" exceeded the amount found by quantitative analysis. If no colophony was added to the sample under examination, then the amount of rosin acids can be determined by *Twitchell's* method (see p. 625). If, however, colophony also was added, then an approximate estimation only can be made with the aid of the numbers set out in the last table.

Coal Tar Oils.—The oils falling under this head boil between 240° and 350° C. They are freed for the most part from naphthalene and anthracene by cooling, and from phenols by washing with caustic soda. They are used as such as lubricants in gas suction pumps or as ingredients of lubricating greases, and are employed as adulterants of painters' varnishes and in lubricating oils.

Their specific gravities are above 1·00.

The indications furnished by the specific gravity test alone are of very limited value if a mixture of two of the described classes of oils, or even all three, be present. The following methods for further examination are available :—

The most reliable test for the detection of **rosin oil** in mineral oil, provided the rosin acids have not been removed in the preparation of the unsaponifiable matter, is, as the author can testify from his own experience, the *Liebermann-Storch* reaction : [1]—

1 to 2 c.c. of the sample under examination are shaken, in a test-tube, with acetic anhydride [2] at a gentle heat ; after cooling, the acetic anhydride layer is drawn off by means of a pipette, and tested by adding one drop of sulphuric acid of 1·53 specific gravity.[3] If rosin oil is present, a fine violet (fugitive) colour is immediately produced.

If less than 1 to 2 c.c. are available, the test can be done on a watch-glass, by stirring the liquid with acetic anhydride and allowing a drop of sulphuric acid to run down the side.

It should be borne in mind that cholesterol gives a similar colour reaction. If, therefore, cholesterol [4] be suspected, the presence of rosin oil would be proved best by examining the mixed fatty acids (obtained from the soap solution) for rosin acids (see below), which always accompany rosin oils.[5] A more complicated method would be to identify cholesterol as the benzoate.

The refractive index of rosin oils $n_{15} = 1{\cdot}535\text{-}1{\cdot}5548$, whereas mineral oils are lower but may reach 1·507. The flash point of rosin oils lies above 250° C.

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[1] For a characteristic colour reaction of pinolin proposed by Grimaldi see Vol. III. Chap. XV. "Varnishes."

[2] It is advisable to ascertain the purity of the acetic anhydride by a blank test.

[3] This acid contains 62·53 per cent of SO_4H_2 ; it is prepared by mixing 34·7 c.c. of conc. sulphuric acid with 35·7 c.c. of water.

[4] Green fluorescence of the liquid, after the violet colour has disappeared, points to the presence of isocholesterol.

[5] Recently rosin oils have appeared in the market, which are so well refined that they do not give the Liebermann-Storch colour reaction.

The quantitative determination of **mineral oil** in mixtures of mineral oil and rosin oils is of practical importance in the examination of lubricating oils. The methods hitherto elaborated will be described under the heading "Lubricating Oils" in Vol. III. Chap. XV.

If rosin oils be absent, and the specific gravity points to the presence of tar oils, the latter may be detected with the aid of nitric acid of specific gravity 1·45.[1] Tar oils exhibit a decided rise of temperature on mixing with this acid, whereas mineral oils become but slightly warm. It is best to ascertain by a preliminary test whether a violent reaction takes place or not, as the size of apparatus to be chosen for the experiment depends on the result. 7·5 c.c. of the sample are placed in a graduated tube, cooled to 15° C., and 7·5 c.c. of nitric acid, specific gravity 1·45, previously cooled to 15° C., are added. The tube is closed by a cork, provided with a thermometer, and the contents are shaken thoroughly. The rise of temperature is then read off. If a strong reaction has occurred, it is advisable to employ smaller quantities, and to proceed as in *Maumené's* temperature reaction test (see p. 479). The same reaction has been proposed by *McIlhiney*[2] for the detection of rosin oil in a mixture of this oil with mineral oils.

The qualitative detection of rosin oils by means of their optical rotation will be dealt with under the headings "Linseed Oil" (Vol. II. Chap. XIV.) and "Lubricating Oils" (Vol. III. Chap. XV.).

Recently *Valenta*[3] proposed a method based on the observation that dimethylsulphate[4] dissolves coal tar hydrocarbons readily at the ordinary temperature and is miscible with them in all proportions, whereas it does not dissolve petroleum hydrocarbons in the cold. The further observation that dimethylsulphate has a very slight solvent action upon rosin oils in the cold led *Valenta* to propose dimethylsulphate as a suitable reagent for separating aromatic hydrocarbons from aliphatic hydrocarbons, and for determining quantitatively their respective proportions in a mixture. *Valenta's* directions are as follows: Place in a stoppered 100 c.c. cylinder, graduated in $\frac{1}{2}$ c.c., an accurately measured volume of the mixture add one and a half volumes of dimethylsulphate, shake for one minute, and allow to stand at the ordinary temperature until two layers have formed. Read off the increase of the dimethylsulphate layer, and calculate this to coal tar oils. Check experiments made by *Valenta* with mixtures of (1) petroleum hydrocarbons and coal tar oils, (2) rosin oil and coal tar oil, (3) petroleum hydrocarbons, rosin oil, and coal tar oil, gave very satisfactory results for coal tar oils.

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[1] Brenken, *Zeits. f. analyt. Chem.*, 1879, 546.

[2] *Journ. Amer. Chem. Soc.* 16, 385.

[3] *Chem. Zeit.*, 1906, 266.

[4] Dimethylsulphate $SO_2(OCH_3)_2$ has the specific gravity 1·334 at 15° C. and boils at 188° C. It should be noted that dimethylsulphate is poisonous. Besides the aromatic hydrocarbons there are also soluble in dimethylsulphate: Nitro-benzene, nitro-toluene, phenol, cresols, and all bases; ether also is readily soluble in dimethylsulphate. Olive oil, rape oil, and cotton seed oil form an emulsion with dimethylsulphate, which gradually deepens in colour to brown, and separates in a short time into two turbid layers. Glycerol behaves similarly, but does not become coloured brown. (Harrison and Perkin.)

The oil dissolved by the dimethylsulphate can be recovered by boiling the solution with alcoholic [1] soda or potash, diluting the saponified mass with water and extracting with ether, in the same manner as the unsaponifiable matter is determined. Thus the quantitative determination of tar oils in mineral oils would become feasible. Dilution of those lubricating oils which are too thick to permit their being shaken up with dimethylsulphate (*e.g.* with nitro-benzene which is soluble in dimethylsulphate) cannot be recommended, as *Harrison and Perkin* [2] have shown that erroneous results are obtained.

According to *Graefe*,[3] *Valenta's* reagent is useful in the case of high-boiling petroleum oils, but fails in the case of low-boiling petroleum distillates as they are very appreciably soluble in dimethylsulphate. Thus a mixture consisting of coal tar benzene and a little petroleum ether gave no separation after treatment with dimethylsulphate, the solution being even capable of dissolving more petroleum ether. *Graefe's* experiments with petroleum oils, lignite tar oils, and various mixtures are set out in the following tables: [4]—

Solubility of Petroleum Oils in $1\frac{1}{2}$ Volumes of Dimethylsulphate

Kind of Oil.	Specific Gravity.	Boiling Point. °C.	Per cent dissolved.
Petroleum ether . . .	0·651	72% from 37 to 85	12
,, . . .	0·708	75% ,, 46 ,, 100	15
,, . . .	0·735	97% ,, 74 ,, 126	15
Russian petroleum . . .	0·821-0·822	94% ,, 139 ,, 300	6
American burning oil, "water white" . . .	0·790	93% ,, 144 ,, 300	4
American burning oil, "standard white" . . .	0·799	80% ,, 121 ,, 300	4
Galician petroleum . . .	0·805	81% ,, 119 ,, 300	7
Paraffin oil	0·890	...	0

Solubility of Lignite Tar Oils in $1\frac{1}{2}$ Volumes of Dimethylsulphate

Kind of Oil.	Specific Gravity.	Boiling Point. °C.	Per cent dissolved.
Petroleum ether . . .	0·792	96% from 127 to 200	20
Solar oil	0·827	98% ,, 144 ,, 235	30
"Cleaning oil" . . .	0·859	95% ,, 194 ,, 250	29
Pale paraffin oil . . .	0·864	74% ,, 205 ,, 300	15
Red oil	0·879	76% ,, 202 ,, 300	24
Gas oil	0·892	81% ,, 200 ,, 300	29
Heavy paraffin oil . . .	0·918	30% ,, 226 ,, 300	18
Extra heavy paraffin oil . .	0·933	4% ,, 250 ,, 300	20

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[1] Aqueous solutions cause bumping.

[2] *Analyst*, 1908, 7.

[3] *Chem. Rev.*, 1907, 112.

[4] *Analyst*, 1908, 2.

Solubility of Mixtures of Coal Tar Benzene with Petroleum Ether in $1\frac{1}{2}$ Volumes of Dimethylsulphate

Benzene in Mixture. Per cent.	Per cent dissolved.
10	22
20	30
30	45
40	60
50	76
60	92
70	100
80	100
90	100

Solubility of Mixtures of Light Coal Tar Oil with Russian Petroleum[1] *in $1\frac{1}{2}$ Volumes of Dimethylsulphate*

Light Coal Tar Oil in Mixture. Per cent.	Per cent dissolved.
10	12·5
20	20·0
30	30·0
40	40·0
50	50·0
60	61
70	75
80	85
90	97

Solubility of Mixtures of Heavy Coal Tar Oil with Gas Oil from Petroleum in $1\frac{1}{2}$ Volumes of Dimethylsulphate

Heavy Coal Tar Oil in Mixture. Per cent.	Per cent dissolved.
10	11
20	20
30	30
40	39
50	50
60	60
70	70
80	81
90	91

---

[1] This Russian petroleum was soluble in $1\frac{1}{2}$ volumes of dimethylsulphate to the extent of 6 per cent (see 1st table).

Solubility of Mixtures of Heavy Coal Tar Oil with Heavy Lignite Tar Oil in 1½ Volumes of Dimethylsulphate

Heavy Coal Tar Oil in Mixture. Per cent.	Per cent dissolved.
10	25
20	29
30	39
40	49
50	59
60	69
70	79
80	89
90	98

Harrison and Perkin,[1] whilst confirming *Graefe's* results with regard to low-boiling petroleum hydrocarbons, found that in the case of mixtures of tar oils with American and Russian lubricating oils the volume of extracted tar oil was less than theory demanded, whereas in the case of Roumanian and Galician petroleum oils, as also of Scotch shale oils, the volume of the extracted oil was greater than theory required. This appears to be due to the fact that the Galician and Roumanian petroleum oils, as also shale oils, are more soluble in dimethylsulphate than are American and Russian oils. (In the case of Galician and Roumanian oils, at least, this would find its explanation in the fact that these oils are comparatively rich in aromatic hydrocarbons.)

Although *Valenta's* method does not yield quantitative results,[2] it must be considered a decidedly useful qualitative method.

In applying *Valenta's* method it should never be omitted to examine the dissolved oil separately, as thereby useful indications may be gathered.

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[1] *Analyst*, 1908, 2.

[2] In *Harrison and Perkin's* opinion the results are so erratic that quantitative result seem to be only accidental.

CHAPTER X

DETECTION AND QUANTITATIVE DETERMINATION OF ROSIN

1. Properties of Rosin

Common rosin or *colophony* [1] is the residue obtained on heating turpentine (pine rosin)—*i.e.* the sap obtained by " tapping " pine trees—in a still until all the moisture and the oil of turpentine (" oil of turps ") is distilled off. The distillation is frequently supported by passing a current of steam through the heated mass. After driving off the " oil of turps," the steam is shut off and the melt in the still is heated for some little time, so that the mass may remain completely amorphous after cooling in the casks into which it is run in the hot state, and in which it solidifies. Colophony forms a light yellow to dark brown transparent mass, the colour of which depends on the manner in which the distillation has been conducted and on the temperature which obtained during the distillation process.[2]

French rosin (from *Pinus maritima*) is known in commerce by the name " galipot." [3] The various qualities of American rosin [4] are distinguished by the letters of the alphabet. " A " is almost black. As the letters ascend in the alphabet, the rosins represented by the different letters are paler and more transparent. " W," or " W.G." (" window glass "), or " W.W." (" water white ") are the palest and

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[1] From *Kolophon*, a town in which rosin was distilled.

[2] Cp. Schwalbe, *Zeits. f. ang. Chem.*, 1908, 1852 ; Walker, Wiggins, and E. C. Smith, *Technolog. Quarterly*, Sept. 1905.

[3] Cp. Coffignier, *Manuel du Fabricant de Vernis.*

[4] For a survey of the turpentine industry in the United States cp. " Report on the Turpentine Industry in the United States," No. 647, *Diplomatic and Consular Reports*, 1906. The following data may be of general interest :—

Export of Rosin from the United States of America, valued in Dollars

	1902.	1903.	1904.	1905.	1906.
England . . .	1,423,853	1,462,804	1,882,280	1,704,185	2,238,386
Germany . . .	902,758	1,076,646	1,858,017	2,025,866	2,842,288
Holland . . .	330,786	417,305	612,091	803,008	1,010,478
Russia . . .	196,003	431,123	271,831	196,726	275,054
Belgium . . .	180,915	249,611	141,936	157,450	227,097
Aústria-Hungary .	148,231	102,775	226,859	275,546	531,304
Total . .	4,202,104	4,817,205	6,021,870	7,060,084	9,899,080

most transparent qualities. During recent years Spanish rosin is being imported into this country in considerable quantities. For further data as to rosins of different origin see Vol. III. Chap. XV. " Varnishes."

Rosin possesses vitreous lustre ; it is very brittle, and breaks with shallow conchoidal fracture. The specific gravity of colophony or common rosin—or shortly " rosin "—varies from 1·045 to 1·085 at 15° C. The melting points of different rosins vary considerably, this depending on the amount of rosin oil in the colophony. Some varieties soften at 70° C., and become semi-fluid in boiling water ; others melt at 99°-100° C., or even at 120°-140° C. Rosin does not melt, however, to a clear liquid, like fats and fatty acids do. On warming, rosin emits a pleasant terebinthinate odour ; at a higher temperature, it burns with a dense yellow and sooty flame, sending forth a very characteristic smell.

On subjecting rosin to destructive distillation, " rosin spirit," " pinolin," and " rosin oil " are obtained as distillates, whilst coke is left behind.

Rosin oils are differentiated in the trade as " soft," " medium," and

Exports of Rosin from the United States of America in Tons *

1902-3	269,009
1903-4	271,808
1904-5	242,789
1905-6	241,243
1906-7	270,990
1907-8	277,707
1908-9	229,336
1909-10	209,934
1910-11	225,624
1911-12	253,916
1912 (7 months, April-October)	151,785

Exports of Rosin from France in Tons *

1903	23,326
1904	30,897
1905	59,382
1906	37,888
1907	37,931
1908	49,230
1909	57,234
1910	55,751
1911	58,789
1912 (11 months)	67,098

Imports of Rosin into Great Britain from all Sources in Tons *

From	1902.	1903.	1904.	1905.	1906.	1907.	1908.	1909.
United States	79,015	81,542	71,816	58,425	66,043	66,295	55,989	50,310
France	13,584	2,486	17,860	17,902	11,793	11,780	19,056	14,610
Spain	..	..	..	3,429	3,589	3,454	4,890	4,495
Portugal	..	..	..	..	..	..	1,550	803
All other countries	318	510	726	775	1,111	1,279	641	781
Total	92,917	84,538	90,402	80,531	82,536	82,808	82,126	70,999

For further data and for the exports of rosin from Spain see Vol. III. Chap. XV. under "Oil of Turpentine."

* These numbers are taken from a circular of Messrs. James Watt and Son, London.

"hard" oils. "Soft" rosin oil is obtained by slow distillation and contains a small amount of rosin acids.

"Hard" rosin oil is obtained by rapid distillation, when larger quantities of rosin acids are carried over mechanically.

The "soft" oil is used for making axle grease, whereas the "hard" oil finds application in the production of lubricating oils by admixture with anthracene oils.[1]

By distillation of rosin *in vacuo*, a hydrocarbon (colophene ?) and an acid $C_{30}H_{32}O_2$ (isosylvic acid) were obtained.[2]

Rosin is insoluble in water but dissolves easily in alcohol, 1 part of rosin requiring no more than 10 parts of 70 per cent alcohol for complete solution. The alcoholic solution has an acid reaction. The acid can be neutralised by titration with alkali, using phenolphthalein as an indicator. Rosin is also soluble in methyl alcohol, amyl alcohol, ether, benzene, acetone, chloroform, carbon bisulphide, carbon tetrachloride,[3] and oil of turpentine. Most of its constituents dissolve in petroleum spirit, the percentage of insoluble matter varying from 1 to 20 per cent in different samples. Solutions of rosin do not leave a grease-spot on paper.

Colophony contains varying quantities of "unsaponifiable matter," viz. hydrocarbons, due to the partial breaking up of the acid on distilling pine rosin. The following table shows how widely different in this respect commercial rosins are :—

Origin.	Unsaponifiable.	Observer.
	Per cent.	
French	15·2	Jean
American "W.W." .	7·34	Evans and Black
,, "W.G." .	5·00	,,
,, "N." . .	9·00	,,
,, "N." . .	8·21	,,
,, "M." . .	7·61	,,

The quantitative methods used in the analysis of oils, fats, and waxes have also been applied to the examination of rosin, since rosin is frequently found in admixture with oils, fats, and waxes, and the commercial products derived therefrom. The examination and determination of rosin is of especial importance in the analysis of soaps. In the following table the author has collated some numbers obtained by the methods described in Chap. VI. It should, however, be distinctly understood that these numbers can only be looked upon as defining the limits within which a given sample may fall. It may be stated as a general rule that the darker a rosin is, the smaller is the difference between its saponification and neutralisation values. This will be gathered by examining the numbers given in Column III. of the table.

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[1] *E. von Boyen*, German patent 210,830, obtains from rosin by treating it with (30 per cent of its weight of) syrupy phosphoric acid, a uniform product boiling at 350° C. without any lower boiling hydrocarbons being produced. This rosin oil is stated to have a very faint odour only ; cp. also K. Bosch, French patent 357,391 ; O. Sprenger, French patent 399,760 ; English patent 5978, 1909 ; C. P. Ogilvie and G. Mitchell, Swedish patent 52,277 ; J. Ljubarski, French patent 414,919 ; English patent 13,128, 1910. A distillation "run" with rosin "C" has been described by F. Schulz, *Chem. Revue*, 1909, 186. With regard to recent developments of the distillation process see T. W. Pritchard, *Journ. Soc. Chem. Ind.*, 1912, 418.

[2] Bischoff and Nastvogel, *Berichte*, 1890, 1919 ; *Journ. Soc. Chem. Ind.*, 1890, 927 ; cp. also French patent 409,026, L. B. Castets.

[3] Cp. C. Baskerville and H. S. Riederer, *Journ. Ind. Eng. Chem.*, 1912 (4), 645.

Kind of Rosin.	I. Neutralisation Value.	II. Saponification Value.	III. Difference, II.-I.	IV. Iodine Value.	Observer.[1]
Austrian . .	146·0	167·1	21·1	116·8	v. Schmidt and Erban[2]
,, . .	130·4	146·8	16·4	109·6	,,
Austrian, pale .	163·0	...	...	...	Kremel[3]
,, dark .	151·0	...	...	...	,,
American . .	173·0	...	...	...	,,
,, . .	169·0	...	...	...	,,
,, . .	181·0	...	...	178·9[4]	Mills[5]
American "W.W."	151·1	183·6	29·5	92·4-93·5	Lewkowitsch[6]
,, "W.G.".	161·4	178·9	17·5	113-114	,,
,, "W.G.".	163·3	184·3	21·0	104-107	,,
,, "W." .	161·3	191·3	30·0	62-64	,,
,, "V." .	164·6	194·0	30·0	55-58	,,
,, "F." .	159·0	174·7	15·7	111-113	,,
French (Galipot) .	138·65	174·76	36·11	121·5-123·5	,,
American "F." .	153·8-169·4	165·2-176·1	5·5-11·8	...	Weger
,, "N." .	157·3	174·3	17·0	168·4[7]	Smetham and Dodd
,, "W.G.".	160·1	177·3	17·2	165·9	,,
,, "W.W."	154·5	174·3	19·8	158·5	,,
,, "Wite".	160·8	177·6	16·8	184·7	,,
,, "Nemo"	162·0	176·4	14·4	181·0	,,

Spanish rosin simulates in its characteristics French rosin (*Galipot*). *McIlhiney* showed that the iodine number varies with the time allowed for the absorption and with the excess of iodine used, to a much greater extent than is the case with oils and fats, and he therefore concluded that the *Hübl* process does not furnish useful results in the examination of rosin. This is indeed borne out by the numbers given in the two following tables :—

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[1] Cp. also C. G. Schwalbe and E. Kinderling, *Journ. Soc. Chem. Ind.*, 1911, 1398.

[2] *Journ. Soc. Chem. Ind.*, 1889, 308. [3] Wagner's *Jahresbericht*, 1886, 443.

[4] Calculated from the bromine value 112·7 by multiplying by $\frac{127}{80}$.

[5] *Journ. Soc. Chem. Ind.*, 1886, 222.

[6] *Ibid.*, 1903, 505, and unpublished experiments. These iodine numbers were determined with *Hübl's* solution, which was allowed to act for six hours. Cp. also C. Ahrens, *Zeits. f. öffentl. Chem.*, 1908, 463.

[7] *Hübl* iodine solution was used and allowed to act for eighteen hours (*Journ. Soc. Chem. Ind.*, 1900, 101).

Iodine Absorption of Rosin from Hübl Solution[1]

	Iodine Number (Hübl).			
	After 2 hours.	After 4 hours.	After 18 hours.	After 7 days.
Rosin "W.W." . .	115·5	124·1	158·5	165·3
,, "N." . .	114·3	125·3	168·4	
,, "W.G." . .	115·5	121·7	165·9	

Iodine Absorption of Rosin from Wijs' Solution

	After	Absorption.	Observer.
Rosin "N."	10 minutes	171·2	Smetham & Dodd
	20 ,,	177·5	,,
	30 ,,	183·6	,,
	1 hour	194·8	,,
	18 hours	249·4 ; 249·4	,,
	48 ,,	270·5	,,
Rosin "N."	2 hours	165·3	Lewkowitsch
	24 ,,	172·2	,,
,, "W."	2 ,,	159·9	,,
	24 ,,	195·8	,,
,, "W.G."	2 ,,	219·0	,,
	10 ,,	214·2	,,
	18 ,,	216·0	,,
	24 ,,	237·7	,,

McIlhiney[2] prefers, therefore, to apply the bromine absorption method described above (Chap. VI. p. 394) to the examination of rosin. From the results obtained with two specimens of rosin ("W.G." and "E."), *McIlhiney* concluded that the absorbed bromine is entirely taken up by substitution. Hence the *bromine addition value* of rosin would be practically *nil*. In further support of his contention that the bromine absorption numbers for rosin lead to more definite numbers than does the iodine absorption by *Hübl's* process, *McIlhiney*[3] published some numbers which I collate in the following table. In order to show the discrepancy between the bromine and the iodine numbers more clearly, I have calculated (see Column II.) the observed bromine absorption numbers to iodine numbers, by multiplying the former by $\frac{127}{80}$.

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[1] Smetham and Dodd, *Journ. Soc. Chem. Ind.*, 1900, 101.

[2] *Journ. Amer. Chem. Soc.*, 1894, 275.

[3] *Ibid.*, 1902, 1109.

Bromine Absorption of a Sample of American Rosin, "W.G."

Time.		Bromine Absorption. I.	II.	III. Iodine Absorption. Per cent.
		Experiment. Per cent Bromine.	Calculated to Iodine Absorption.	(Found by Hübl's Method.)
hours.	mins.			
0	2	160·8	255·3	
0	18	174·5	277·0	
1	0	...	...	126·7
1	9	178·0	282·6	
2	0	...	...	133·1
4	0	...	...	142·0
8	0	...	...	144·8
18	0	...	...	160·3
20	0	213·4	338·8	
52	0	...	...	172·6

Experiments made in the author's laboratory show, however, that commercial rosins do possess, besides substitution numbers, definite addition numbers, as will be gathered from the following table, to which have been added the iodine absorption numbers found by the *Wijs* modification of the *Hübl* method.

Unfortunately, on using the *Wijs* solution substitution numbers cannot be ascertained, as the action of acetic acid on potassium iodate is very different from that of mineral acids; hence widely varying results are obtained according as the concentration and the time during which the acetic acid is allowed to act on the iodate vary.

Bromine and Iodine Absorptions of Common Rosins (Lewkowitsch)

Rosin.	Bromine Values.			Time during which Bromine was allowed to act.	Iodine Value. (Wijs' Solution.)			
	Total Absorption.	Addition.	Substitution.		After 2 hours.	After 10 hours.	After 18 hours.	After 24 hours.
"W.G."	210·7	41·14	84·78	½ hour	219·0	214·2	216·0	237·7
	211·6	49·68	80·96	,,				
	202·5	59·92	71·29	1 hour				
	203·5	88·42	57·54	,,				
"N."	146·9	87·6	29·65	½ hour	165·3	...	...	172·2
	145·7	108·06	18·82	,,				
	148·1	92·84	27·63	1 hour				
	145·2	107·7	18·75	,,				
"W."	201·8	114·0	43·9	½ hour	159·9	...	...	195·8
	201·6	104·96	48·42	,,				
	197·2	78·24	59·48	1 hour				
	191·8	85·14	53·33	,,				

The high neutralisation values of rosins prove conclusively that colophony is not, as *Maly* maintained,[1] an anhydride (viz. abietic anhydride), but consists chiefly of free acids and small quantities of anhydrides.

The same conclusion has been arrived at by *Perrenoud*.[2] According to him colophony does not contain abietic anhydride. In the case of American colophony (from trunks of *Pinus strobus* and *Pinus picea*, and from the root of *Pinus sylvestris*) the crystals are said to be *abietic* acid, whereas in "galipot" and in rosin from the trunk of *Pinus sylvestris* they are stated to consist of the isomeric *pimaric* acid. To both acids the same formula $n(C_{10}H_{14}O)$ is ascribed; pimaric acid is most likely $C_{40}H_{56}O_4$, as follows from the analysis of its crystalline ammonium salt. Both abietic and pimaric acids are optically active, and rotate the plane of polarised light to the left.[3] The specific rotatory powers of abietic and pimaric acids are stated by *Perrenoud* to be 48° and 56° respectively; *Köhler*[3] recently found for pimaric acid the composition $C_{20}H_{30}O_2$ and $[\alpha]_D^{20} = -280{\cdot}5^\circ$.

The *sylvic* acid of some authors is in *Liebermann's* opinion [4] identical with abietic acid. His researches, continued by *Haller*,[5] led to the result that pimaric acid is optically inactive. *Vesterberg*,[6] again, expressed (in 1885) the opinion that three distinct acids are coexistent in "galipot."

Mach,[7] rejecting the formulæ given above for abietic, sylvic, and pimaric acids, stated that these acids are identical, and proposed for *abietic acid* (the name which he retained) the formula $C_{19}H_{28}O_2$. This formula was derived from numerous ultimate analyses and determinations of the molecular weight of specimens of the acid prepared by different methods from various specimens of colophony. According to *Fahrion*,[8] however, *Mach's* abietic acid is identical with sylvic acid $C_{20}H_{30}O_2$. The formula $C_{20}H_{30}O_2$ is confirmed by *Levy*,[9] who showed that *Easterfield and Bagley's*,[10] as also *Tschirch* and *Studer's* [11] advocacy of *Mach's* formula is not supported by conclusive evidence based on analysis. The acid $C_{20}H_{30}O_2$ melted after repeated recrystallisation from methylalcohol, at 182° C. (*Levy*). The formula $C_{20}H_{30}O_2$ has been further confirmed by *Vesterberg*,[12] *Koritschoner*,[13] and for lævo-pimaric acid and sapinic acid (in *Picea excelsa*) by *Köhler*.[14]

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[1] *Journ. f. prakt. Chem.* 96, 145. Earlier investigations are briefly summarised by G. B. Frankforter in *Journ. Amer. Chem. Soc.*, 1909, 561.

[2] *Chem. Zeit.*, 1885, 1590.

[3] With regard to lævo-pimaric and sapinic acid (in the rosin from *Picea excelsa*, Lk.) cp. S. Leskiewicz, *Journ. f. prakt. Chem.*, 1910 (81), 403; J. Köhler, *Chem. Zentralbl.*, 1911 (2), 1598; *Journ. f. prakt. Chem.*, 1912 (85), 523.

[4] *Berichte*, 17, 1885.

[5] *Ibid.*, 18, 2167.

[6] *Ibid.* 18, 3334.

[7] *Journ. Soc. Chem. Ind.*, 1893, 1044.

[8] *Zeits. f. ang. Chem.*, 1901, 1197; 1902, 83. Cp. also Henry, *Journ. Chem. Soc.*, 1891, 1144; Fahrion, *Zeits. f. ang. Chem.*, 1904, 239, 1907, 356; and Klason and Köhler, *Journ. f. prakt. Chem.*, 1906 (73), 337.

[9] *Zeits. f. ang. Chem.*, 1905, 1740; *Berichte*, 1906, 3043; 3658.

[10] *Journ. Chem. Soc.*, 1904 (85), 1238.

[11] Cp. Tschirch and Studer, *Arch. d. Pharm.* 241, 495; *ibid.* 245, 380. Cp. also Schkateloff, *Monit. Scient.*, 1908, 217; *Journ. Chem. Soc.*, 1908, Abstr. i. p. 816.

[12] Berichte, 1907, 120.

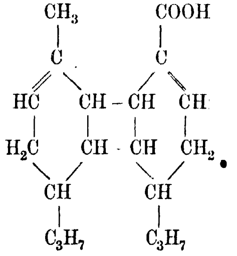
[13] *Zeits. f. ang. Chem.*, 1907, 641.

[14] *Journ. f. prakt. Chem.*, 1912 (85), 560.

Frankforter[1] states that he obtained from the rosin of the Norway pine, *Pinus resinosa*, an acid having the formula $C_{25}H_{38}O_5$—"resinic acid"—melting at 97-98° C., and "abietic" acid to which he still ascribes the composition given by *Mach*, viz. $C_{19}H_{28}O_2$, although he states distinctly that the analyses also agree with the formula $C_{20}H_{30}O_2$.

Abietic (*sylvic*) *acid*, $C_{20}H_{30}O_2$, is obtained in a pure state in the form of crystals by digesting 1 part of coarsely powdered colophony with 2 parts of 70 per cent alcohol at a temperature of 50°-60° C. The crystalline powder which separates is purified by recrystallisation from 3 parts of boiling 70 per cent alcohol. *Levy* (see above) prefers to recrystallise from methylalcohol.[2] Another method is to pass hydrochloric acid gas through an alcoholic solution of colophony, when abietic acid separates (*Flückiger*[3]). According to *Mach*, abietic acid occurs in colophony in varying amounts; some specimens contain 90 per cent of the crude acid; from others no acid could be isolated. On treating an alcoholic solution of colophony with water, a precipitate of impure abietic acid is obtained, which remains suspended in the liquid, forming an emulsion with it. On adding a dilute mineral acid and warming subsequently, rosin separates in the form of globules on the side of the containing vessel, so that the clear liquid can be poured off. The rosin thus obtained is at first very viscid, but regains its former consistence after repeated boiling with water, or by heating to incipient fusion. In its pure state abietic acid crystallises in laminæ or small crystals melting at 182° C. (*Levy*). The crystals are soluble in alcohol, ether, benzene, and glacial acetic acid. Abietic acid is not converted into an anhydride on heating.

Abietic acid contains one carboxyl group and two pairs of doubly-linked carbon atoms. This is expressed by the constitutional formula proposed by *Fahrion*:[4]—



Vesterberg records 77 as the iodine value of abietic acid. Theory requires for two pairs of doubly-linked carbon atoms 168·2. It has been shown above that rosin does not absorb the full amount of iodine, and it would therefore seem desirable to repeat the absorption test with bromine. Colophony, especially if exposed in the form of a fine powder, takes up oxygen from the air. According to *Fahrion*,[1] peroxides are formed which are said to be very unstable.

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[1] *Journ. Amer. Chem. Soc.*, 1909, 561.

[2] Cp. also German patent 221,889 (P. Levy).

[3] *Journ. f. prakt. Chem.* 101, 235; *Jahresb. d. Chem.*, 1867, 727.

[4] *Chem. Revue* 1911 239.

In agreement with *Fahrion's* formula is *Levy's*[2] observation that on oxidation of abietic acid with permanganate in alkaline solution four hydroxyl groups are added, leading to an acid of the formula $C_{20}H_{34}O_6$ (*Fahrion's* tetrahydroxy-sylvic acid[3]). This acid melts at 240°-245° C., is soluble in ether and acetone, less readily soluble in glacial acetic acid and absolute alcohol, sparingly soluble in benzene and ethylacetate, insoluble in petroleum ether. It crystallises from acetone and dilute alcohol in transparent, well-formed crystals melting with evolution of water at 246°-247° C. The yield of the acid is very small.[4]

On warming colophony with dilute caustic alkalis, it is readily dissolved with formation of salts—rosinates or pinates—which resemble in many respects the alkali soaps made from oils and fats. Hence the alkali salts are termed " rosin soaps." Thus the solutions of the alkali salts are hydrolysed by water (as can be shown experimentally with the aid of phenolphthalein; see p. 135) and lather on being agitated. The " rosin soaps " are also thrown up (" salted out ") from their aqueous solutions, by addition of concentrated alkali or of common salt. However, the separation does not take place so readily and so completely as in the case of soaps made from fatty acids. Dilute mineral acids liberate the rosin acids from their soaps.

The sodium salt of rosin dissolves readily in alcohol, as also in ether containing alcohol; in pure ether, however, it is but sparingly soluble. According to *Barfoed*, 29 c.c. of ether dissolve within twenty-four hours 0·0239 grm., and 19 c.c. after eight days dissolve 0·041 grm. of sodium rosinate.

The solutions of the rosinates of the alkali metals yield insoluble precipitates with solutions of the salts of the alkaline earths and heavy metals. On the solubility of some of these salts in alcohol and ether, methods for separating the rosin acids from the fatty acids have been based. The zinc,[3] copper, silver, and manganese rosinates are soluble in ether; calcium rosinate is insoluble in this menstruum. Further data on the metallic salts will be found in Vol. III. Chap. XV.

In the quantitative analysis of a rosin soap the acid is separated as free rosin acid (" abietic acid "); it is therefore necessary in accurate analysis (as will be shown in Vol. III. under " Analysis of Soaps "), for the proper calculation of the composition of soap, to convert the weight of the rosin acids found into the weight of the original colophony. From the table p. 618 it will be seen that rosin can be determined by titration with standard alkali solutions. This is best done in alcoholic solution. From the formula $C_{20}H_{30}O_2$ it follows that 302 parts of abietic acid combine with 56·1 parts of potassium hydrate to form a rosinate neutral to phenolphthalein. Its neutralisation value is therefore 185·7. Since colophony contains anhydrides and also unsaponifiable substances besides free acid, the mean combining weight of rosin acids deviates from 302. From a large number of experiments made with commercial rosins the rule has been derived that the mean combining weight may be taken, for practical purposes, as 346.

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[1] *Zeits. f. ang. Chem.*, 1907, 356; cp. also *Chem. Revue*, 1911, 239.

[2] *Berichte*, 1909, 4305.

[3] Cp. German patent 166,563.

[4] Cp. also H. Endemann, *Amer. Chem. Journ.*, 1905 (33), 523.

Since rosin does not consist of pure abietic acid, but contains, besides other not yet identified bodies, from 10 to 20 per cent of substances behaving like anhydrides, the weight of "rosin" separated by decomposing its sodium salt with mineral acids is slightly higher than that of the original rosin converted into sodium soap. A measure of the difference may be derived from experiments by *Smetham and Dodd*, who saponified rosin with an excess of aqueous caustic soda, decomposed the resulting soap with a slight excess of dilute sulphuric acid, and separated the insoluble rosin acids by means of ether.[1] In the following table I collate the neutralisation and saponification numbers of the original rosins with the numbers found for the recovered acids after the rosins had passed through the saponification process :—

Kind of Rosin.	Original Rosin.			Recovered Rosin after Saponification.		
	Neutralisation Value.	Saponification Value.	Difference.	Neutralisation Value.	Saponification Value.	Difference.
American "N.". .	157·3	174·3	17·0	159·1	165·5	6·4
,, "W.G." .	160·1	177·3	17·2	161·0	169·5	8·5
,, "W.W." .	154·5	174·3	19·8	159·1	167·5	8·4
,, "Wite" .	160·8	177·6	16·8	163·9	176·4	12·5
,, "Nemo" .	162·0	176·4	14·4	163·9	175·3	11·4

2. Detection and Determination of Rosin in Neutral Fats and in Waxes

The older analytical methods based on the ready solubility of rosin in alcohol do not lead to satisfactory results. The most reliable method for the detection of rosin, which the author recommends as thoroughly trustworthy, is the *Liebermann-Storch* reaction described above (see p. 610). In case the colouration is indistinct, owing to the dark colour of the sample, it is advisable to saponify it with alcoholic potash, liberate the fatty acids together with the rosin acids by acidulating, and examine the mixed fatty and rosin acids.

To perform the test, the acids are dissolved in acetic anhydride at a gentle heat, and the solution is cooled. Sulphuric acid of 1·53 specific gravity[2] is then carefully allowed to flow into the solution, when the presence of the minutest quantity of rosin acid will be indicated by the appearance of a reddish-violet colouration ; if the solution be too warm, this colour will disappear almost immediately, changing into a brownish-yellow. In any case, the colour disappears quickly. Fatty acids do not give the violet colour ; but it should be remembered that cholesterol, which might be present amongst the mixed acids, exhibits a similar reaction with acetic anhydride and sulphuric acid. In that event the cholesterol must be removed by shaking out the soap solution with ether previous to the liberation of the mixed fatty and rosin acids. This reaction may be also used for the detection of rosin in beeswax. It should, however, be noted that rosin acids which have been treated with strong hydrochloric acid (as in the *Twitchell* method, see below) no longer give a distinct reaction in the *Liebermann-Storch* test.[1]

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[1] Cp. also Henriques, *Chem. Revue*, 1899, 110.

[2] Sulphuric acid of 1·53 sp. gr. contains 62·53 per cent of SO_4H_2; it is prepared by mixing 34·7 c.c. of conc. sulphuric acid with 35·7 c.c. of water.

In mixtures of neutral oils with rosin (*e.g.* linseed oil and rosin), the author determines the rosin approximately by titrating an accurately weighed quantity of the sample, dissolved in ether-alcohol, with standard alkali, using phenolphthalein as an indicator. The combining weight adopted for rosin is 346 ; the amount of free fatty acids of the oil is neglected, its value being, as a rule, very small as compared with the acid value due to the presence of rosin. Experiments carried out on mixtures of linseed (and cotton seed) oil with rosin gave very satisfactory results.

If greater accuracy be desired, the rosin acids must be separated off together with the mixed fatty acids, and examined as described under the following head.

3. Quantitative Determination of Rosin Acids in Admixture with Fatty Acids

Lewkowitsch [2] has shown that the older methods proposed by *Barfoed* and by *Gladding*, and the modifications thereof, do not lead to reliable results. A description of these methods is therefore omitted here, and *Twitchell's* method only is described as it yields the best results. A combination of *Gladding's* and *Twitchell's* methods was proposed by *Holde*,[3] but since the suggested corrections appear to me somewhat arbitrary, this method also is omitted here.[4]

Twitchell's [5] method is based on the property of the aliphatic acids to become converted into their ethylic ester when acted upon in alcoholic solution by hydrochloric acid gas, whereas rosin undergoes very little change under the same treatment (see p. 622). The analysis is carried out as follows :—

Two to three grms. of the mixed fatty and rosin acids are weighed off accurately in a flask, dissolved in ten times their volume of *absolute* alcohol (with weaker alcohol the conversion of fatty acids into esters is not complete), and a current of dry hydrochloric acid[1] gas passed through the solution, the flask being cooled by immersion in cold water. The gas is rapidly absorbed at first, and after about forty-five minutes, when unabsorbed gas escapes, the operation is finished. To ensure complete esterification the flask is allowed to stand for an hour. The ethylic esters and the rosin acids separate on the top as an oily layer. The contents of the flask are then diluted with five times their volume of water, and boiled until the aqueous solution has become clear. From this stage the analysis may be carried out either (*a*) volumetrically, or (*b*) gravimetrically.

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[1] M. J. Sans describes (*Ann. Chim. anal. appl.*, 1909 (14), 140) a sensitive colour reaction for rosin obtained with methyl sulphate ; cp. also P. Foerster, *ibid.*, 1909, 14.

[2] *Journ. Soc. Chem. Ind.*, 1893, 503.

[3] *Mitteil. a. d. Königl. Techn. Versuchsanst.*, 1902, 41.

[4] For the description of the earlier quantitative methods, the reader is referred to the second edition of this work.

[5] *Journ. Soc. Chem. Ind.*, 1891, 804.

(*a*) *The Volumetric Method.*—The contents of the flask are transferred to a separating funnel, and the flask is rinsed out several times with ether. After vigorous shaking the acid layer is run off, and the remaining ethereal solution, containing the mixed ethylic esters and rosin acids, washed with water until the last trace of hydrochloric acid is removed. 50 c.c. of alcohol are then added, and the solution is titrated with standard caustic potash or soda, using phenolphthalein as an indicator. The rosin acids combine at once with the alkali, whereas the ethylic esters remain practically unchanged. The number of c.c. of normal alkali is multiplied by 0·346, and this gives the amount of rosin acids in the sample.

(*b*) *The Gravimetric Method.*—The contents of the flask are mixed with a little petroleum ether, boiling below 80° C., and transferred to a separating funnel; the flask is washed out with the same solvent. The petroleum ether layer should measure about 50 c.c. After shaking, the acid solution is run off, and the petroleum ether layer washed once with water, and then treated in the funnel with 45 c.c. of a one-fifth normal solution of KOH and 5 c.c. of alcohol. The petroleum ether solution of the ethylic esters will then be found to float on the top, the rosin acids having been extracted by the dilute alkaline solution with formation of rosin soap. The soap solution is run off, decomposed with hydrochloric acid, and the separated rosin acids are collected as such, or preferably are dissolved in ether and isolated after evaporating the solvent. The residue, after drying and weighing, gives the amount of rosin acids in the sample.

Of all the methods proposed hitherto for the estimation of rosin acids in mixtures thereof with fatty acids, *Twitchell's* process yields the best results. They must not, however, be considered as strictly accurate. *Lewkowitsch*[2] has shown, by an exhaustive examination of both the volumetric and gravimetric processes, that they only yield approximately correct results.

Since the mean combining weights of different brands of commercial rosin vary within considerable limits (cp. p. 618), there adheres to the volumetric analysis an uncertainty from which the gravimetric analysis is free. Under the action of the hydrochloric acid rosin undergoes some destruction[1] with the formation of acids of lower molecular weight, since the volumetric method gave, as a rule, too high results. In the gravimetric process, again, some of these secondary products pass into the aqueous solution without being dissolved by the petroleum ether. By subsequent extraction with ether, part of the dissolved substances may be recovered, but even then the results of the gravimetric analysis were found too low. Of course, the unsaponifiable oils occurring in rosin (p. 617) remain in the petroleum ether solution and thus escape weighing. But even this does not wholly account for the considerable deficit.

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[1] The proposal made by H. Wolff to substitute sulphuric acid for hydrochloric acid cannot be recommended, cp. Fahrion, *Chem. Revue*, 1911, 241.

[2] *Journ. Soc. Chem. Ind.*, 1893, 504.

The subjoined tables, detailing analyses of mixtures of oleic acid and rosin acids of previously ascertained combining weight, confirm the author's critical remarks :—

Volumetric Analysis (*Lewkowitsch*)

Oleic Acid.	Rosin.	1/1 KOH used.	Mixture contains Rosin Acids. Combining Weight 346.		Calculated for the yield of Rosin Acids only.	
			Theory.	Experiment.	Theory.	Experiment.
Grms.	Grms.	c.c.	Per cent.	Per cent.	Per cent.	Per cent.
2·5096	0·8027	2·4	21·234	24·90	100·0	100·60
2·3988	0·8167	2·56	25·398	27·35	100·0	105·50
1·5638	1·5532	4·41	49·83	48·40	100·0	95·60
1·4006	1·5202	4·19	52·047	48·93	100·0	92·81
0·8918	2·5198	6·68	73·86	66·397	100·0	89·47
0·8296	2·5298	6·72	75·305	67·81	100·0	89·45

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[1] The results given in the above table are confirmed by experiments made later by *Evans and Black*, as is shown by the following table :—

Weight of Rosin.	Rosin calculated from Titration.	Loss.
Grms.	Grms.	Per cent.
2·0968	2·054	2·00
2·4723	2·45	0·90
2·035	..	0·93
2·03	..	0·69
2·115	..	1·14

[TABLE

Gravimetric Analysis (Lewkowitsch)

No.	Oleic Acid.	Rosin.	Found Rosin Acids.	Mixture contains Rosin Acids.		Calculated for yield of Rosin Acids.	
				Theory.	Experiment.	Theory.	Experiment.
	Grms.	Grms.	Grms.	Per cent.	Per cent.	Per cent.	Per cent.
1	2·4666	0·8199	0·7385	24·947	22·32	100	87·65
2	2·8058	0·8577	0·7736	23·412	20·98	100	87·80
3	1·6465	1·5342	1·3200	48·234	40·96	100	83·73
4	1·4090	1·5092	1·3128	51·716	44·35	100	84·65
5	0·8600	2·5252	2·0930	74·595	60·58	100	80·66
6	0·8430	2·5322	2·1744	75·023	63·12	100	83·56
7	...	4·2524	3·5631	...	...	100	83·44
8	...	4·6864	3·8334	...	...	100	81·46
9	...	4·6700	3·8979	...	...	100	83·12

The following tables will furnish an indication as to how far, in practical cases, the results obtained by either process approximate to the theoretical ones.

The "mixed fatty and rosin acids" were obtained from soaps specially prepared on a large scale from carefully weighed quantities of fats and rosins. Average samples of the fats and rosins were examined separately for the yield of fatty acids from the former and for the combining weight of the latter, such determinations being indispensable for a correct calculation of the theoretical amount of rosin acids.

Volumetric Analysis (Lewkowitsch)

Mixed Fatty and Rosin Acids.	Rosin Acids.	
	Theory.	Experiment.
No.	Per cent.	Per cent.
1	9·79	9·98, 9·34, 9·795, 9·91.
2	19·69	23·97, 24·55, 22·93, 23·28, 23·98, 24·08.
3	21·45	24·96, 24·78, 23·63.
4	24·66	24·89, 25·15, 25·06, 24·28.
5	30·31	29·69, 30·12, 28·18, 29·78.
6	39·81	40·24, 40·37, 41·44, 42·13, 41·8, 40·37, 42·18, 40·55, 40·07, 40·05, 43·69, 41·12, 41·81, 40·77, 44·82.
7	45·05	45·76, 46·50, 49·61, 47·66, 46·45, 47·84, 45·34, 44·24, 44·48, 44·39.

Gravimetric Analysis (*Lewkowitsch*)

Mixed Fatty and Rosin Acids.	Rosin Acids.	
	Theory.	Experiment.
No.	Per cent.	Per cent.
1	9·79	9·38, 9·97.
2	19·69	20·46, 20·55, 19·96,[1] 19·99, 19·44, 19·33.
3	21·45	19·25, 18·27, 19·37, 17·83,[1] 19·54, 18·61, 18·57, 19·16.
4	24·66	20·97, 16·65, 21·76.
5	30·31	25·76, 25·06, 23·66, 26·10.
6	39·81	35·97, 38·86, 36·44, 36·14, 35·42, 35·86, 32·51, 36·29.
7	45·05	37·58, 37·23, 37·29, 36·97, 35·32, 40·06, 36·8.

By washing the petroleum ether solution with alkali a second time, and extracting the acid layer with common ether, the following results were obtained :—

Mixed Fatty and Rosin Acids.	Rosin Acids.				
	Theory.	Experiments.			
		Extracted by First Alkali Wash.	Extracted by Second Alkali Wash.	Extracted by Ether.	Total.
No.		Per cent.	Per cent.	Per cent.	Per cent.
2	19·69	19·46	0·115	1·045	20·62
2	19·69	18·44	0·074	0·822	19·34
3	21·45	19·14	0·105	0·3615	19·607
3	21·45	19·19	0·061	0·2839	19·54
4	24·66	21·72	0·179	1·203	23·102
4	24·66	22·29	0·239	1·01	23·54
5	30·31	25·75	0·019	2·41	28·18
5	30·31	26·93	0·085	0·72	27·73
6	39·81	34·96	1·296	1·567	37·80
6	39·81	34·596	0·190	1·12	35·91

Should the rosin originally admixed with the fat contain notable amounts of (unsaponifiable) rosin oils, the latter are determined as described under 4.

It should be pointed out that in the case of impure oxidised oils such as black grease, by the treatment with hydrochloric acid gas a notable amount of acids are obtained, which must not be taken to be rosin acids without further investigation. *A. A. Besson*[1] records the same observation for sulphur olive oil (cp. Vol. II. "Olive Oil").

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[1] Emulsion.

4. Quantitative Determination of Rosin Acids in Admixture with Fats (or Fatty Acids) and Unsaponifiable Matter

If a mixture of rosin acids, fat, and unsaponifiable matter be under examination, the sample is saponified by boiling with alcoholic potash, and the alcohol driven off by prolonged boiling after dilution with water. Disregarding any undissolved unsaponifiable matter, the aqueous solution of soap is transferred to a separating funnel and shaken out with petroleum ether; thus the unsaponifiable matter is removed. The soap solution yields, on treatment with a mineral acid, a mixture of fatty acids and rosin acids, which are then separated by *Twitchell's* process.

On applying *Twitchell's* volumetric method, the separation of the unsaponifiable matter may be avoided by the following procedure:[2]— The mixture is saponified with alcoholic potash, and the rosin acids, fatty acids, and unsaponifiable matter isolated by acidulating. If a mixture of the acids and unsaponifiable matter be given at the outset, saponification is, of course, unnecessary.

Two grams of the mixed acids and unsaponifiable matter are weighed off accurately, titrated with normal caustic soda or potash, and the number of c.c. necessary to establish neutrality to phenolphthalein is noted. Another 2 grms. are treated with hydrochloric acid gas, as described above, and titrated with normal alkali. If a be the number of c.c. used in the first experiment, and b the number found in the second experiment, then we find, adopting 346 as the combining weight for rosin, and 275 for fatty acids (palmitic, stearic, oleic):—

1. Weight of rosin acids $= b \times 0{\cdot}346$.
2. Weight of fatty acids $= (a - b) \times 0{\cdot}275$.
3. Weight of unsaponifiable $= 100 - [b \times 0{\cdot}346 + (a - b) \times 0{\cdot}275]$.

The accuracy of the result will, of course, greatly depend on the correctness of the assumed combining weights 346 and 275.

5. Separation of Rosin Acids from Fatty Acids

The separation of rosin acids from fatty acids is effected by passing the mixture of rosin and fatty acids through the esterification process described under *Twitchell's* method. We then have a mixture of free acids and esters, and after titration, as *e.g.* in the volumetric process, there results a mixture of rosin soap and ethyl esters of the fatty acids. Now, if the alcohol is distilled off and the remaining mixture is treated with water, the soap is dissolved, leaving the esters floating on the surface of the soap solution. The two layers are separated, and the soap solution, after washing with common ether to remove the last traces of dissolved ethylic esters, yields the rosin acid on acidulating. The ethylic esters are saponified by means of caustic alkali, and the fatty acids separated in the usual manner. Both the rosin acids and the fatty acids may then be examined separately.

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[1] *Chem. Zeit.*, 1912, 814; 1913, 453.

[2] *Journ. Soc. Chem. Ind.*, 1891, 804.

CHAPTER XI

APPLICATION OF THE FOREGOING METHODS TO THE SYSTEMATIC EXAMINATION OF NATURAL OILS, FATS, AND WAXES

An attempt is made in this chapter to describe in what manner the methods detailed in the foregoing chapters can be employed in the examination of a given sample, with a view to identifying it, or ascertaining its nature. It may be stated at the outset that in the present state of our knowledge we are not yet in possession of a definite course of analysis, to be followed in all circumstances, such as is the case in inorganic qualitative and quantitative analysis. Yet by adopting a systematic plan of examination, it is possible in the majority of cases to identify a given sample of a natural oil, fat, or wax, and to ascertain whether it is a pure or adulterated specimen. In the latter case the nature of the adulterant can generally be ascertained.

It must be distinctly understood that the following notes refer to *natural* products only. With the introduction of "hydrogenised" ("hardened") fats (see Vol. III. Chap. XV.) such distinguishing features as consistence, colour, odour, and taste, have lost much, if not the whole, of their former value.

The **consistence** at the ordinary temperature helps to limit conveniently the range of substances to which examination must extend.

Colour also proves in many cases of some assistance, chiefly in the case of solid fats (most oils in their refined state have a bright yellow colour). Thus amongst the solid fats, laurel oil is recognised by its yellowish-green colour, crude palm oil by its red colour (shading off from the brightest red of Lagos oil to a dirty dark red of Congo oil), and beeswax by its characteristic dirty yellow colour.

The **odour** and also the **taste** of a sample will, as a rule, give some clue as to its nature. These "organoleptic" methods require, however, a good deal of practical experience, which is more frequently possessed by dealers in oils than by analytical chemists. Still, it is easy to discriminate the marine animal oils from other oils by their characteristic **smell**.[1] Also rape oil, olive oil, lard oil, cotton seed oil, and linseed oil are readily recognised by their smell, especially when slightly warmed.

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[1] Cp. Tsujimoto, "On the Cause of the Odours of Oils and Fats, especially of Marine Animal Oils," *Journ. Colleg. Eng.*, Tokyo, Imp. Univ., 1908, iv. (5), 181.

In some cases it is even possible to recognise adulterants, such as rosin or mineral oils. Greater practice is required for the recognition of certain oils or fats by **taste**; linseed oil, maize oil, and cotton seed oil can be thus identified. Also lard and tallow can be readily recognised. *Rancidity* is readily ascertained by **taste** in the case of edible oils and fats. **Taste** is therefore of great importance in the examination of these products, as taste alone is the ultimate criterion in deciding whether a sample is rancid or not. A cultivated sense of taste is required for giving an opinion as to the value of a particular brand of edible oil which is pure in the sense of being wholly free from adulterants. To take an example, taste alone can discriminate between the finest olive oils of the south of France, the somewhat " harder " oils of Tuscany, and the harsh oils of south-eastern Italy.

If a mixture of two oils or fats is under examination, the preliminary indications furnished by consistence, colour, etc., frequently lose their importance. Yet with the help of the methods described in the foregoing chapters, it is, as a rule, possible to ascertain the presence and to recognise the nature of both constituents of the mixture, at least qualitatively. Frequently it will even be feasible to determine quantitatively the proportions in which the component parts have been mixed.

A more difficult problem is presented by a mixture of three or more oils, fats, or waxes. In cases of this kind commercial analysis may not always lead to a satisfactory result; still it is possible in the majority of cases to identify at least one or two of the individual constituents in a mixture.

Correct interpretation of indications afforded by the tests applied, and strict logical reasoning, enable us in the majority of cases to narrow down, by a process of elimination, the range of possible constituents of a mixture to such an extent that the practised analyst will but rarely be confronted with the impossibility of arriving at least at approximate accuracy. If in the course of a commercial analysis the limits of our present knowledge have been reached, the application of methods that have not yet been used for the case under consideration will suggest itself. This happens not infrequently in the examination of technical products derived by the processes described in Vol. III. Chapter XV., and will play a very important part in the analysis of " hydrogenised " oils and fats. In such cases the analysis will assume the nature of a scientific investigation.

One of the most important problems required to be solved by commercial analysis is whether a sample is pure or sophisticated.

Adulteration of saponifiable oils, fats, and waxes with unsaponifiable oils or solid hydrocarbons is easily detected. The object of sophistication being, of course, to cheapen an article, only those oils, fats, or waxes are used as adulterants that are lower in price than the oil, fat, or wax to be adulterated. Hence, the examination of a totally unknown mixture of oils, fats, or waxes will be greatly facilitated by learning its price, for thereby a number of more expensive substances is excluded from the scope of the analysis. In order to assist in fixing the attention on the substances lower in the scale of prices than the sample under examination, the following list, ranged in the order of the commercial values of oils, fats, and waxes, may be found useful. It should, however, be borne in mind that these prices are subject to wide fluctuations from year to year, causing *e.g.* cotton seed oil, linseed oil, castor oil, and rape oil, to change places. Olive oil and cotton seed oil stand very far apart in the following list, yet at the end of 1909 low-class edible olive oils came very near in price to edible cotton seed oil. As another example may be quoted that the market value of linseed oil in the spring of 1913 was about half of that ruling in 1910.

Oils and Liquid Waxes

Almond oil
Sperm oil
Olive oil
Neat's foot oil
Lard oil
Cod liver oil
Arctic sperm oil
Arachis oil
Poppy seed oil
Sesamé oil
Seal oil
Rape oil
Castor oil
Cotton seed oil
Soya bean oil
Maize (corn) oil
Linseed oil
Whale oil
Japan fish oil, Menhaden oil
Cod oil
Mineral oil
Rosin oil
Tar oils

Fats and Waxes

Cacao butter
Butter fat
Wool wax
Beeswax
Carnaüba wax
Chinese wax
Lard
Cocoa nut oil
Palm nut oil
Tallow
Palm oil
(Paraffin wax)
Bone fat; other waste fats
Wool grease

The object of technical analysis is reached in the readiest possible manner by adopting a systematic plan, based broadly on the application of the general methods described in the preceding chapters.

If a specific oil, fat, or wax be under examination, it is advisable to consult first the description of that oil, fat, or wax, and especially the tables containing the characteristic numbers, given in Vol. II. Chapter XIV. An endeavour will be made there to conclude the description of most of the individual oils, fats, and waxes by pointing out those adulterants that fall within the range of practical consideration, and then indicating the methods of detecting them. In short, each individual product will be considered as an analytical problem. It must, of course, be borne in mind that commercial oils, fats, and waxes vary, in the case of vegetable products, with the soil, climate, and chiefly the species of plant, and, in the case of animal products (sometimes to a very considerable extent) according to the race of the animal, the mode of feeding, etc. The following examples will illustrate this point:—Some years ago olive oils having a higher iodine value than 85 or 87 would certainly have been considered as adulterated; yet Californian, Dalmatian, and Tunisian olive oils of undoubted purity have been found to absorb more iodine. Therefore, olive oils can no longer be condemned on the strength of a high iodine value alone. Extremely instructive in the same respect are the commercial lards, especially those of American origin. Whereas some years ago a lard having the iodine value of 63-65 would have raised the presumption of adulteration, there are at present coming into the market lards having iodine values which largely exceed these limits. Such lards must be allowed to pass muster, since it has been recognised that the fattening of hogs (especially in the United States and Canada) with cotton cake and (or) corn (maize) produces "soft lards."

Beeswaxes, the acid and saponification values of which deviated considerably from the numbers 20 and 95 respectively would have been judged, up to the last twenty years, as being undoubtedly adulterated; yet considerable quantities of Indian and Chinese waxes are imported in which the proportion of free acid is considerably smaller, and consequently the amount of saponifiable esters much larger than in those waxes which had been known up till now in European establishments.

If it be borne in mind that adulteration has almost become a fine art, and that it is being practised with the full armour of scientific knowledge by experts who are frequently some years ahead of the knowledge possessed by the analytical chemist, it will readily be understood that the analyst must select special methods and tests and adapt them to each special case.

The plan followed in the description of general methods (Chaps. V.-X.) will furnish an outline, and approximately indicate the sequence of methods to be applied in the examination of a given sample.

OILS AND FATS

It is advisable, in the first instance, to derive the fullest information by testing the oils and fats themselves; after that the examination of the fatty acids may be attacked. In the following lines some typical examples will be considered.

1. Determination of Neutral Fat and Free Fatty Acids in a given Sample—Acid Value and Saponification Value

This is a frequently occurring problem, as in the valuation of a "soap stock fatty acid," or to ascertain how far saponification of a neutral fat has proceeded in the control of a technical saponification process in order. Let k, the saponification value of a sample of autoclaved tallow, be 203·0, and a its acid value 162·2. Then the difference $k - a = 203{\cdot}0 - 162{\cdot}2 = 40{\cdot}8$ corresponds to the neutral fat present in the sample. Since the saponification value of neutral tallow may be taken once for all as 195, we have the proportion :—

$$195 : 100 :: 40{\cdot}8 : x \text{ ; hence } x = \frac{40{\cdot}8 \times 100}{195} = 20{\cdot}92.$$

The percentage of neutral fat in the sample is therefore 20·92, and the proportion of free fatty acids $100 - 20{\cdot}92 = 79{\cdot}08$.

Even if the saponification value of the original fat be unknown, there is no need for operating with weighed quantities. Take a conveniently large—not weighed—sample and determine in one and the same sample the number of c.c. normal alkali required for the neutralisation and saponification values respectively. Let a and b be the numbers found, then $\frac{a \times 100}{b}$ gives the proportion of free fatty acids.

The free fatty acids may also be determined gravimetrically; this becomes necessary in the case of a mixture of free fatty acids derived from one kind of fat, with a neutral fat of another kind. In that case several grms. of the sample are weighed off or measured in a flask, hot alcohol and phenolphthalein are added, and the free fatty acids neutralised carefully by running in standard alkali until the solution just acquires a permanent pink colour. The liquid is allowed to cool, diluted with an equal volume of water (taking care that the proportion of alcohol does not fall below 40 per cent), and shaken out in a separating funnel with ether or petroleum ether as described Chap. VI. p. 457, "Unsaponifiable Matter." The aqueous layer is drawn off, and the ether layer repeatedly washed with water. The ethereal solution yields, after evaporation of the solvent, **the neutral fat.** From the aqueous layer the free fatty acids are separated by means of mineral acid; their weight may be determined as described Chap. VIII. p. 522. Their mean molecular weight may then be determined, as also the mean molecular weight of the fatty acids in the neutral fat, after saponifying the latter and isolating the liberated fatty acids.

If the mean molecular weight of the free fatty acids be known from the outset, their quantity can be determined without weighing, by calculating the amount from the number of c.c. of normal potassium hydrate used in the neutralisation of the free fatty acids.

The next important step in the examination of a given sample is to determine its **iodine value.** In many cases the results will permit to establish definitely the nature of the natural oil or fat. Simultaneously, the state of freshness or of rancidity may be ascertained, provided, of course, no unsaponifiable matter be present. If this be suspected, the determination of the *unsaponifiable matter* may be combined with the determination of the saponification value, as shown above (Chap. VI.).

The following example may illustrate the foregoing remarks.

2. Edible Oil

An edible oil yielded the following numbers on examination :—

Acid value	3·2
Saponification value . . .	196·1
Iodine value	109·3
Unsaponifiable	0·82 per cent.

From these numbers the conclusion is derived that the sample is practically a completely saponifiable oil, which cannot belong to the rape oil group. Its iodine value points to cotton seed oil. Taking 282 as the mean molecular weight, which differs very slightly from the actual mean molecular weight of the fatty acids of cotton oil given in the table Chap. VIII. p. 514, it is calculated, with the aid of the conversion table Chap. VI. p. 440, that the sample contains 1·6 per cent of free fatty acids.

A decided colouration in the *Halphen* test would confirm the conclusion that the oil under consideration is cotton seed oil.

If a mixture of **two oils**, the nature of which is known or can be readily identified, is under examination, it is possible to calculate approximately the proportion of both oils, provided the difference of their iodine values is sufficiently large. The following example may illustrate this.

3. Edible Oil

An edible oil, sold as olive oil, gave on examination the following numbers :—

Acid value	3·2
Saponification value . . .	196·1
Unsaponifiable matter . . .	0·82 per cent.
Iodine value	93

The iodine value being rather high for olive oil, the presumption of adulteration is raised immediately. The presence of oils of the rape oil group is excluded by the saponification value. The presence of almond oil is excluded by its price. Reference to the table of the iodine values p. 410 would suggest the presence of either cotton seed oil or arachis oil. If the *Halphen* colour test (Vol. II. Chap. XIV. "Cotton Seed Oil") has revealed the presence of cotton seed oil, its proportion in the sample may be calculated with the aid of the following two equations. Let x be the percentage of olive oil and y the percentage of cotton seed oil, then we have $x + y = 100$. Taking the mean iodine values of olive oil and cotton seed oil as 85 and 109 respectively, we obtain the second equation

$$\frac{85x}{100} + \frac{109y}{100} = 93. \quad \text{Hence } x = 66{\cdot}6 \text{ per cent.}$$

If the *Halphen* test for cotton seed oil has been negative, the sample must be examined for the presence of arachidic acid. If such has been found, then the calculation therefrom to arachis oil will approximately furnish the proportion of arachis oil. In this case the calculation of the constituent oils from the iodine values (by means of two equations as shown above) would obviously lead to very uncertain results.

For the examination of "Hydrogenised Fats" (Hardened Fats) see Vol. III. Chap. XV.

If a high saponification value of a sample has directed attention to the presence of **soluble fatty acids,** then the *Reichert* value, and, if need be, the determination of the insoluble acids in conjunction with the unsaponifiable matter, will be of material assistance. This may be illustrated by the calculation of the approximate composition of a sample of butter fat (see **4**).

4. Butter Fat

The following numbers were found in the examination of a butter fat:—

Acid value	0·56
Reichert-Meissl value	28·1
Insoluble acids + unsaponifiable . . .	87·5 per cent.
Iodine value	32·6
Mean molecular weight of the insoluble fatty acids	260
Stearic acid in the insoluble fatty acids . .	0·49 per cent.

From the low acid value the conclusion is drawn that mono- and di-glycerides are practically absent.

From the mean molecular weight of the insoluble fatty acids, 260, the mean molecular weight of the corresponding glycerides is calculated as $3 \times 260 + 38$[1] $= 818$. The percentage of glycerides of insoluble fatty acids is therefore 91·8 per cent, as calculated from the following proportion:—

$$(3 \times 260) : 818 :: 87{\cdot}5 : x ; \; x = 91{\cdot}8 \text{ per cent.}$$

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[1] $C_3H_2 = 38$; $[C_3H_5.(OH)_3 = C_3H_2 + 3H_2O]$.

The glycerides of insoluble fatty acids consist of laurin, myristin, palmitin, stearin, traces of arachin, and olein (linolin being assumed to be absent).

The following calculation from the iodine value 32·6 leads to the percentage of olein = 37·82 :—

$$86·2 : 100 : : 32·6 : x ; \ x = 37·82.$$

The amount of stearic acid in the insoluble fatty acids was found = 0·49 per cent, corresponding to 0·51 per cent of stearin [$(3 \times 284) : 890 : : 0·49 : x$]. This corresponds to 0·46 per cent of stearin in the butter fat. Since the glycerides of volatile fatty acids make up the difference, the composition of the butter fat under examination may be preliminarily taken to be as follows :—

Stearin	0·46 per cent
Laurin, myristin, palmitin, arachin . .	53·52 ,, ,,
Olein	37·82 ,, ,,
Butyrin, caproïn, etc. (by difference) .	8·20 ,, ,,
	100·00 ,, ,,

A further insight into the nature of the volatile acids may be gained from the amount of potassium hydrate required to saturate the total volatile fatty acids obtained by the process described p. 529. The experiment gave 41·4 mgrms. potassium hydrate (the value corresponding to the above-given *Reichert-Meissl* value is 31·47) per grm. of butter fat. The volatile acids from 100 grms. of butter fat would therefore require 4·14 grms. KOH. The mean molecular weight of the volatile fatty acids could be calculated, if their absolute weight were known. This can be derived from the weight of their glycerides found above (by difference) as 8·20 per cent. Since $3 \times 56·1 = 168·3$ parts of potassium hydrate correspond to 92 parts of glycerol (in the absence of mono- and di-glycerides), or to 38 parts of C_3H_2, the 4·14 grms. KOH correspond to

$$\frac{38 \times 4·14}{168·3} = 0·93 \text{ grm. of } C_3H_2.$$

The percentage of the volatile fatty acids in the sample is therefore $8·20 - 0·93 = 7·27$. Since 7·27 grms. of the mixed volatile acids required 4·14 grms. of KOH, their mean molecular weight must be

$$M : 56·1 : : 7·27 : 4·14. \quad M = 98.$$

From the numbers given in the following table it must be concluded that lauric and capric acids can only be present in very small quantities, whereas butyric and caproic acids preponderate :—

Acid.	Formula.	Molecular Weight. Theory.
Butyric . .	$C_4H_8O_2$	88
Caproic . .	$C_6H_{12}O_2$	116
Caprylic . .	$C_8H_{16}O_2$	144
Capric . .	$C_{10}H_{20}O_2$	172
Lauric . .	$C_{12}H_{24}O_2$	200

Further information with regard to the composition of the glycerides of volatile acids will be given under "Butter Fat" (Vol. II. Chap. XIV.).

If the *Reichert-Meissl* value of the butter fat were 24 or even 26, it would become necessary to examine the sample for the possible presence of cocoa nut oil or (and) palm kernel oil. This would involve the determination of the amount of alkali required for the neutralisation of *the insoluble fatty acids* (see p. 424), and in doubtful cases the application of the *Phytosteryl acetate test* (see Chap. IX. p. 588 and p. 642).

In more complicated cases, such as are presented by a mixture of three oils or fats (cp. "Margarine" Vol. III. Chap. XV.), the examination of the insoluble fatty acids becomes imperative. The first information will be gained by the determination of their melting and solidifying points and of their mean molecular weight. Next their iodine value will be determined. I have endeavoured in Chapter VIII. to indicate a systematic course of examining the mixed fatty acids, and the reader may therefore be referred to p. 498. It is only necessary to supplement the directions given there by some additional explanations.

In the first instance, recourse will be had to the separation of the solid from the liquid fatty acids. The amount of unsaturated fatty acids contained in the former will be determined next by the iodine value. In most cases it will be accurate enough to calculate from the iodine value to oleic acid, and correct the mean molecular weight of the saturated fatty acids accordingly.

If stearic acid be present, it should be determined in a direct manner (if possible). If a mixture of two acids of known composition be under examination, their respective proportions may be derived *approximately* by calculation from the mean molecular weight of the mixed acids, provided this number has been determined with great accuracy.

The mean molecular weight of the mixed fatty acids, M, should be determined with not less than 5 grms. of substance. Letting x and y be the percentages, and M_1 and M_2 the respective molecular weights of the fatty acids, then x and y can be calculated from the following equations:—

$$x+y=100,$$

$$\frac{M_1x}{100}+\frac{M_2y}{100}=M.$$

For practical purposes, *e.g.* in works where mixtures of known fatty acids are examined frequently, it is advisable to construct a table such as the following, which has been calculated by *Mangold* for stearic and palmitic acids :—

Neutralisation Values of Mixed Stearic and Palmitic Acids

Neutralisation Value. Mgrms. of KOH per 1 grm.	Mean Molecular Weight.	100 parts of the mixture contain	
		Stearic Acid.	Palmitic Acid.
197·5	284	100	—
198·5	282·6	95	5
199·5	281·2	90	10
200·5	279·8	85	15
201·5	278·4	80	20
202·5	277·0	75	25
203·5	275·6	70	30
204·6	274·2	65	35
205·6	272·8	60	40
206·7	271·4	55	45
207·77	270·0	50	50
208·86	268·6	45	55
209·95	267·2	40	60
211·06	265·8	35	65
212·18	264·4	30	70
213·30	263·0	25	75
214·45	261·6	20	80
215·60	260·2	15	85
216·77	258·8	10	90
217·95	257·4	5	95
219·13	256·0	—	100

If more than two fatty acids are present, the method yields unreliable results.

The examination of the **liquid fatty acids** is a more complicated problem. In the present state of our knowledge the examination will, in the first instance, be confined to the qualitative detection of oleic, linolic, linolenic, and clupanodonic acids. The last-named acid occurs in marine animal oils. If oleic, linolic, and linolenic acids have been detected qualitatively in a drying oil, it is possible to calculate *approximately* their proportions from the mean molecular weight of the liquid fatty acids and their iodine value, both numbers being found by direct determinations. Let M be the molecular weight of the mixed liquid fatty acids, M' the molecular weight of oleic acid (282), M'' the molecular weight of linolic acid (280), and M''' the molecular weight of linolenic acid (278). Further, let I be the iodine value of the mixed liquid fatty acids, I' the iodine value of oleic acid (90·07), I'' the iodine value of linolic acid (181·42), and I''' the iodine value of linolenic acid (274·1). Then the percentages x, y, and z of the three acids may be calculated from the following three equations :—

$$x+y+z=100,$$
$$I'x+I''y+I'''z=100\,I,$$
$$M'x+M''y+M'''z=100\,M.$$

It must, however, be distinctly understood that these calculations should only be looked upon as furnishing rough approximations, and they should only be employed if no other method is available. At best they should only be used to confirm results obtained by quantitative methods, such as the proportion of bromine in the brominated acids (see Chap. VIII., where a systematic course of examining the mixed liquid acids is outlined).

For the examination of the **unsaponifiable matter** it is necessary to isolate a quantity sufficient to perform the tests described in Chapter IX. One of the most important operations under this head is the **phytosteryl acetate test.**

5. Detection of Vegetable Oils and Fats in Oils and Fats of Animal Origin—Phytosteryl Acetate Test

This test becomes of importance in the examination of lard for vegetable oils and fats, especially when a high iodine value of the sample raises the presumption of adulteration with cotton seed oil, and when this presumption has been corroborated by a positive *Halphen* test. The phytosteryl acetate test is further of great importance in the examination of a butter fat in which a small amount of cocoa nut oil or palm kernel oil is suspected.

These two cases will be dealt with exhaustively in Vol. II. Chap. XIV. under the headings " Lard " and " Butter Fat " respectively.

It may be pointed out that the phytosteryl acetate test does not lose its value in the case of " Hydrogenised Fats " (" Hardened Fats ").

6. Detection of Animal Oils and Fats in Oils and Fats of Vegetable Origin[1]

This problem, the converse of the preceding one, resolves itself practically into a separation of cholesterol from (phytosterol) sitosterol. If only small quantities of animal oils or fats have been admixed with a vegetable oil or fat, the problem is a very difficult one. The author has employed the following method with satisfactory results:—The isolated alcohols are converted into their acetates and treated as is done in the phytosteryl acetate test. The acetates contained in the mother liquors from the first and (or) second and third crops of crystals being richer in cholesterol than the original mixture of alcohols, the mother liquors are collected, evaporated down to dryness, and the dry acetates are again passed through the phytosteryl acetate test. The melting point of the first crop of crystals now obtained will indicate presence or absence of cholesterol. If need be, the process must be repeated once more. The author thus obtained sufficiently accurate results in the case of, to him, unknown mixtures of animal and vegetable fats.

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[1] *E.g.* lard oil in olive oil (cp. *Journ. Soc. Chem. Ind.*, 1903, 1153).

For the separation of cholesterol from phytosterol by means of their bromides, the separation of phytosterol from *stigmasterol,* and the separation of *coprosterol* from both cholesterol and phytosterol, and the indication furnished by the "Heat of Bromination Test" see Chap. IX. p. 596.

WAXES

In the examination of Waxes and the products derived therefrom, the investigation of the unsaponifiable matter acquires great importance. The methods applicable in this case have been detailed at length in Chap. IX. p. 600. They may be further illustrated by the following examples :—

1. "Recovered Grease"[1]

(*Crude Wool Fat*)

In a "recovered grease" (cp. Vol. III. Chap. XVI.) the following constituents are determined :—

(*a*) Free fatty acids.
(*b*) Neutral saponifiable matter.
(*c*) Unsaponifiable matter.

(*a*) *Free Fatty Acids*

The amount of alkali required to saturate the free fatty acids in 1 grm. of the "recovered grease" was 0·71 c.c. normal KOH (acid value=39·8). A large weighed quantity of "recovered grease" was then almost completely neutralised with the greater part of the alkali required (as calculated from the acid value) and then carefully titrated with half-normal alkali, until the solution became pink to phenolphthalein. A large proportion of neutral saponifiable matter and unsaponifiable matter rose to the top as an oily layer, and was separated from the soap solution, after having been dissolved in ether. The remainder of the neutral saponifiable matter and unsaponifiable matter was removed from the soap solution by shaking out with ether. The ethereal solutions were united, freed from adhering soap by washing with water, and the solvent was then distilled off. Thus the neutral saponifiable matter (*b*) and the unsaponifiable matter (*c*) were obtained together.

Between the aqueous and the ethereal layers there appeared a flocculent stratum, which was found to consist of a sparingly soluble soap. This was isolated by filtering off from the soap solution. The fatty acids of both the easily soluble soap and the sparingly soluble soap were separated in the usual manner by decomposing with a mineral acid. Thus the free fatty acids of the "recovered grease" were obtained in two fractions, viz. (1) acids forming soluble soaps; (2) acids forming insoluble soaps.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 134 ; cp. also *ibid.*, 1896, 14.

Both groups of acids were found to contain inner anhydrides or lactones, a definite increase of weight on boiling with acetic anhydride (cp. p. 451) having been ascertained; therefore, in order to determine the mean molecular weight, the acids had to be boiled with alcoholic potash. The molecular weights found were respectively 326 and 520. The proportion of the acids (1) to the acids (2) having been found to be 9 : 1, the mean molecular weight of *the total* free fatty acids may be taken as—

$$\frac{9 \times 326 + 520}{10} = 345.$$

On distilling 5 grms. of the "recovered grease" as in *Reichert's* process, it was found that 1 grm. required 0·124 c.c. of normal potash for the neutralisation of the volatile fatty acids. Assuming as their mean molecular weight 102 ($C_5H_{10}O_2$), the "recovered grease" contains $10·2 \times 0·124 = 1·26$ per cent of *free volatile acids.*

The insoluble free fatty acids in 1 grm. were saturated by $0·71 - 0·124$ c.c. $= 0·586$ c.c. of normal potash. Their mean molecular weight being 345, we find $34·5 \times 0·586 = 20·22$ per cent of *insoluble free fatty acids.*

(*b*) *and* (*c*) *Neutral Saponifiable Matter and Unsaponifiable Matter*

A somewhat large quantity of the substance (*b*) and (*c*), prepared as described already, was saponified, and the soap solution tested for *glycerol.* The negative result proved *absence of glycerides.* The neutral saponifiable matter must, therefore, be considered a *wax.*

The ether residue obtained by extracting the saponified mass with ether, and evaporating off the latter, was completely dissolved by acetic anhydride, no oily layer separating on cooling (p. 602). Therefore, *hydrocarbons* were absent, and the *unsaponifiable matter* (*c*) could only consist of alcohols.

The wax (*b*) was separated from the unsaponifiable matter (*c*) by judicious boiling out with alcohol,[1] in which the wax is almost insoluble. The latter was thus obtained as a viscous, wax-like substance, melting to a thick liquid at about 40° C.

On saponification with double normal alcoholic potash under pressure (p. 107), 1 grm. of the wax was found to require 1·825 c.c. of normal potash, or, in other words, its saponification value was 102·4.

The alcohols (*unsaponifiable*) were determined in the usual manner by extracting the saponified mass with ether; the fatty acids were then estimated in the soap solution by the method described in Chap. VIII. p. 523. Thus the composition of the wax was found, in two analyses, as follows:—

---

[1] Preferably acetic anhydride.

	I. Per cent.	II. Per cent.
Fatty acids . .	56·3	54·1
Alcohols .	43·2	44·0
	99·5	98·1

The sum of the constituents of the wax should have been higher than 100, several per cent of water being assimilated on saponification. The deficiency must be looked for in the percentage of the fatty acids, this having been found too low, owing to the property of these acids of easily losing water on drying, with formation of inner anhydrides or lactones. When using *alcoholic* potash for the determination, the molecular weight of these fatty acids was found to be 327·5, from which the percentage composition of the wax may be calculated as follows:—

	Per cent.
Fatty acids, $1·825 \times 32·75 =$	59·77
Alcohols (mean of values of analyses I. and II.) .	43·60
	103·37

The *mean molecular weight of the alcohols* calculated from the equation

$$M = \frac{43·6 \times 327·5}{59·77}$$

was found to be 239.

The fatty acids absorbed only 17 per cent of *iodine*; they consisted, therefore, for the most part of saturated acids.

(c) *Unsaponifiable Matter*

The proportion of unsaponifiable matter was found *approximately* by analysing the mixture of (*b*) and (*c*) in the same manner as (*b*) was examined, and by collating the numbers obtained, in the following manner:—

1 grm. of the mixture of (*b*) and (*c*) required 1·73 c.c. of normal KOH for saponification. Its percentage composition was found as follows:—

	I. Per cent.	II. Per cent.
Fatty acids	50·7	49·8
Alcohols	47·5	47·6
	98·2	97·4

From these numbers we calculate—

	Per cent.
Fatty acids, $1·73 \times 32·75$	56·66
Alcohols	47·55
	104·21

The 56·66 parts of fatty acids require 41·34 parts of alcohols, of the mean molecular weight 239, to form wax. Consequently there are present in the "recovered grease" 47·55 − 41·34 = 6·21 per cent of *uncombined unsaponifiable matter.*

The composition of the "recovered grease" is therefore—

	Per cent.
Volatile fatty acids	1·26
Insoluble free fatty acids	20·22
Unsaponifiable matter (uncombined alcohols)	6·21
Wax (wool wax), by difference	72·31
	100·00

To check the result, the sum of the uncombined alcohols and wax could have been determined direct.

The number 72·31 for wax can be resolved, with the help of its above-given percentage composition (fatty acids, 59·77 per cent; alcohols, 43·60 per cent), into two numbers expressing its component parts, viz. 72·31 × 0·5977 = 41·81 per cent of fatty acids, and 72·31 × 0·436 = 30·5 per cent of alcohols. The total unsaponifiable matter obtainable from the "recovered grease" on complete saponification is, therefore, 30·5 + 6·21 = 36·71 per cent. Hence the analytical result may be expressed as follows:—

		Per cent.	Total unsaponifiable matter.
	Volatile fatty acids	1·26	
	Insoluble free fatty acids	20·22	
	Unsaponifiable matter (uncombined alcohols)	6·21	36·71
Wax	Combined alcohols	30·50	
	Combined fatty acids	41·81	

The percentage of the *total unsaponifiable matter*—36·71—can, of course, be verified by direct determination, which may be suitably combined with the determination of the saponification value. Direct experiment gave the number 36·47 (see below).

A more rapid, and for technical purposes sufficiently accurate, method would be to determine the *acid value*, the *saponification value*, the proportion of *total unsaponifiable matter*, the *mean molecular weight of the total insoluble acids*,[1] and, if required, the *Reichert-Meissl value*. By proceeding in this manner, the following numbers were obtained:—

1 grm. required for the neutralisation of the volatile acids	0·124 c.c. of normal KOH
1 grm. required for the neutralisation of free insoluble acids	0·586 c.c. " "
1 grm. required for the neutralisation of total insoluble acids	2·19 c.c. " "
1 grm. required for the neutralisation of combined insoluble acids (by difference)	1·48 c.c. " "
Mean molecular weight of the total insoluble acids	332[2]
Unsaponifiable matter	36·47 per cent.

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[1] This must be determined with *alcoholic* potash (cp. above).

[2] This number is somewhat too high, owing to the dark colour of the alcoholic solution of the fatty acids.

From these analytical data we find:—The percentage of the free insoluble acids is $0·586 \times 33·2 = 19·45$; the percentage of the combined fatty acids, as hydrated acids, $1·48 \times 33·2 = 49·13$; and the percentage of volatile acids, $0·124 \times 10·2 = 1·26$, as before.

These numbers are collated in the following table:—

	Per cent.
Volatile fatty acids	1·26
Insoluble free fatty acids	19·45
Combined fatty acids (as hydrated acids)	49·13
Total unsaponifiable matter	36·47
	106·31

Part of the surplus over 100 is due to a certain amount of water having been assimilated on saponification; the remainder is due to an error in the number found for the molecular weight of the total insoluble fatty acids, owing to the difficulty of titrating accurately the dark alcoholic solutions.

It would not have been permissible to determine the proportion of the total fatty acids by the method described p. 523, as the result would obviously be too low, owing to the formation of inner anhydrides.

2. Wool Wax[1] ("Lanolin")

Wool wax was dehydrated by melting and allowing the water to subside. The anhydrous wax was then dissolved in absolute alcohol and saponified by means of metallic sodium in a flask attached to an inverted condenser. The alcohol was distilled off, and the mixture of soap and alcohols, whilst still warm, was poured into water, and shaken until the temperature had fallen so that common ether could be added with safety. After vigorous shaking, the mixture was allowed to stand for some days. It then separated into three layers, viz.:—

(1) An ethereal layer on the top, consisting of the ethereal solution of the *alcohols* (unsaponifiable matter).

(2) An aqueous layer on the bottom, being a solution of soap—*easily soluble soap*.

(3) An intermediate thick layer, representing a soap sparingly soluble in water—*sparingly soluble soap*.

The ethereal layer was drawn off, washed well with water, which was later on added to (2) and (3), and the mixture of (2) and (3) exhausted with ether until no more unsaponifiable matter was extracted. Each portion was examined for soap. The first extractions yielded the unsaponifiable matter free from soap; later, small quantities of soap, increasing in inverse proportion to the quantity of unsaponifiable matter, appeared in the extracts. These were treated separately with warm water until free from ash, before being united with the main portion.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1896, 14.

Thus the *alcohols—unsaponifiable matter*—were obtained free from ash.

1. *Alcohols—Unsaponifiable Matter.*—The amount of unsaponifiable matter obtained was 51·84 per cent. It represented an unctuous substance of light yellow colour. The following characteristics were ascertained :—

Melting point	46°-48° C.
Iodine value	26·35
Increase in weight on boiling with acetic anhydride	8·26 per cent
Saponification value of the acetate	153·23

From the following table :—

	Increase on boiling with Acetic Anhydride. Per cent.
Cetylalcohol	17·2
Cerylalcohol	10·6
Cholesterol (or isocholesterol)	10·9

it will be gathered that cetylalcohol must be almost absent. Further, it may be concluded from the low iodine number that the proportion of the two cholesterols cannot be very large, as the iodine value of cholesterol is 67·7.[1]

On subjecting the wool-wax alcohols to treatment with soda-lime and maintaining the temperature at 250° C., about 80 per cent were recovered as unchanged alcohols; 6 per cent of fatty acids, of the melting point 51°-53° C., could be isolated from the soap solution.

2. *Fatty Acids of the Easily Soluble Soap.*—The separation of the easily soluble soap from the insoluble soap, (3), was effected by filtration.

The soap solution was freed from dissolved ether by distillation, and the fatty acids were then isolated in the usual manner by boiling with acid. The amount obtained was 25·5 per cent. The colour of these acids was light reddish-brown.

The following characteristics were determined :—

Melting point	52·5°-56·5° C.
Iodine value	9·95
Neutralisation value	173·88
Saponification value	189·67

The definite difference between the saponification and neutralisation values, viz. 15·79, points to the presence of lactones (see Chap. VIII. p. 517); it was then ascertained that above 120° C. the acids rapidly lose water, whereas the iodine value varies but little.

In another preparation the ether was not removed by distillation but mineral acid was added to the cold solution and more ether added, so that the separated fatty matter was at once transferred to the ether, from which it could be recovered at a low temperature. The fatty matter thus obtained was *white* and showed the following characteristics :—

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[1] *Journ. Soc. Chem. Ind.*, 1892, 143; cp. Chap. IX. p. 604.

Iodine value	10·1
Neutralisation value	168·92
Saponification value	192·82

The difference between the saponification and neutralisation values is in this case larger than before, viz. 25·9, and it thus becomes evident that whereas the iodine value remains practically constant, the lactones are partially converted into fatty acids on heating the mixed acids with water, as was done in the previous case.

The lactones were isolated by carefully neutralising the fatty matter with aqueous potash and exhausting the soap solution with petroleum ether. The fatty acids were liberated from the soap solution in the usual manner. Their neutralisation and saponification values were found to be 194 and 193 respectively.

The examination of the lactones led to the following numbers :—

Iodine value	2·4
Acid value	1·5
Saponification value	174·63

The soap solution obtained from the lactones (anhydrides) by boiling with alcoholic potash was treated with a mineral acid to separate the fatty acid. The acid value of the substance was found to be 61·24, thus proving that lactones had been re-formed to a considerable extent.

3. *Fatty Acids of the Sparingly Soluble Soap.*—The fatty acids were liberated by boiling the soap solution with mineral acid. They had the following characteristics :—

(1) Iodine value	6·95
(2) Neutralisation value	106·5
(3) Saponification value	128·2
(4) Difference (3)-(2)	21·7

In a second preparation the fatty acids were liberated in the cold in the same manner as described above. The isolated fatty matter was sparingly soluble in cold ether or petroleum ether, and large quantities of the solvent were required to effect complete solution. The fatty substance thus obtained was white; its quantity amounted to 26 per cent. It gave the following characteristics :—

(1) Iodine value	3·9
(2) Acid value	86·16
(3) Saponification value	135·86
(4) Difference (3)-(2)	49·70

This portion of the wool wax contains therefore a larger amount of lactones than that described under 2.

The fatty substance was then separated, in the manner described above, into (*a*) fatty acids, and (*b*) lactones.

The fatty acids (*a*) had the following characteristics :—

Iodine value	4·85
Neutralisation value	131·38
Saponification value	141·8
Melting point	65°-66° C.

Hence lactones had again been formed on decomposing the soap. The lactones (*b*) had the following characteristics :—

Iodine value	8·69
Saponification value	115·0

On separating the fatty matter from the alcoholic soap solution by acidulating with a mineral acid, lactones were re-formed to a varying extent in different experiments ; but the re-formation of lactones in this portion of the wool wax took place to a very much smaller extent than was the case in the corresponding portion of the easily soluble soap.

3. "Distilled Grease"[1]

(*Liquid Portion*)

The liquid portion of the distillate obtained on a large scale by subjecting "recovered grease" to distillation gave on examination the following results :—

(*a*) 1 grm. required for the neutralisation of the free fatty acids	1·92 c.c. of normal KOH
(*b*) 1 grm. required for the neutralisation of the total fatty acids on saponification	2·10 c.c. ,, ,,
(*c*) 1 grm. required therefore for the neutralisation of the combined fatty acids	0·18 c.c. ,, ,,
(*d*) Mean molecular weight of the total fatty acids[2] .	300·5
(*e*) Total unsaponifiable matter	38·8 per cent.

From the numbers recorded under (*c*), (*d*), and (*e*) the following composition of the distilled grease may be derived :—

	Per cent.
Fatty acids (as hydrated acids), 2·1 × 30·05 . .	63·1
Total unsaponifiable matter	38·8
	101·9

The low number obtained for the combined fatty acids shows that the greater portion of the wax had been decomposed during distillation.

The free fatty acids were isolated as described p. 643. Their mean molecular weight was 286 ; they may, therefore, be considered as consisting of a mixture of oleic, stearic, and palmitic acids, with a small proportion of higher fatty acids. The proportion of free fatty acids in the "distilled grease" was, therefore, 1·92 × 28·6 = 54·91 per cent.

The wax *plus* the unsaponifiable matter was isolated in the same manner as described p. 644. The separation of these two constituents was, however, impossible, as the unsaponifiable matter is also insoluble in alcohol. The mixture of the two substances was therefore saponified, so as to isolate the fatty acids contained in the wax. These were titrated with *alcoholic* potash and found to have the molecular weight 394. The proportion of combined fatty acids in the "distilled grease" was, therefore, $(2{\cdot}10-1{\cdot}92)\times 39{\cdot}4=7{\cdot}09$ per cent.

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[1] Lewkowitsch, *Journ. Soc. Chem. Ind.*, 1892, 141.

[2] Determined with *alcoholic* potash.

The alcohol combined with the latter acids was contained in the total unsaponifiable matter. Its presence was proved, on the one hand, by boiling an accurately weighed portion with acetic anhydride, and ascertaining that an increase in weight had taken place; and, on the other hand, by isolating the alcohol from the total unsaponifiable matter by means of alcohol.

Adopting the molecular weight of the alcohols that had been found p. 645 for the combined alcohols in the "recovered grease," we can calculate the proportion of *alcohols* from the equation

$$x=\frac{7{\cdot}09\times 239}{394};$$

hence $x=4{\cdot}3$.

The amount of *undecomposed wax* in the "distilled grease" is, therefore, neglecting the small amount of water assimilated on saponification, $7{\cdot}09+4{\cdot}3=11{\cdot}39$ per cent.

The remainder of the unsaponifiable matter, $38{\cdot}8-4{\cdot}3=34{\cdot}5$ per cent, consists of hydrocarbons formed in consequence of the free fatty acids and of the wax of the "recovered grease" having been decomposed during distillation (cp. Vol. III. Chap. XVI.).

The composition of the "distilled grease" is expressed by the following numbers:—

	Per cent.	
Free fatty acids	54·91	
Combined fatty acids . . .	7·09	Undecomposed wax. 11·39
Combined alcohols	4·30	
Unsaponifiable matter (hydrocarbons) .	34·50	
	100·80	

For the further examination of the hydrocarbons, cp. Vol. III. Chap. XVI. "Distilled Grease Oleine."

4. Beeswax

The examination of beeswax may be carried out on the same lines as indicated under "Recovered Grease." Ether is, however, unsuitable as a solvent for the neutral portion of beeswax, and is best substituted by carbon tetrachloride.

The proportion of easily soluble soap is very small in the case of pure beeswax.

The detailed examination of beeswax, and especially of adulterated beeswax or beeswax mixtures, is best carried out by saponifying the sample, diluting the alcoholic solution with one volume of water, and shaking out with ether, when three layers are obtained (cp. p. 644).

(*a*) An ethereal layer (on the top) containing the free alcohols of beeswax, the hydrocarbons present in beeswax (together with any added hydrocarbons), and the alcohols previously combined with fatty acids to form saponifiable esters.

(*b*) An aqueous layer (at the bottom) containing the easily soluble soaps (soaps of palmitic acid, etc.).

(*c*) An intermediate layer containing sparingly soluble soaps (of cerotic, melissic, etc., acids).—This layer must be exhaustively extracted with ether in order to remove completely the occluded unsaponifiable matter.

Each layer is then examined separately by the methods described in the foregoing pages.

For an abbreviated method of examining beeswax, including the detection of other waxes and other adulterants, see Vol. II. Chap. XIV. " Beeswax."

TECHNICAL PRODUCTS

The examination of technical products is illustrated by numerous examples given in Vol. III. Chap. XV. and Chap. XVI.

The investigation of a complicated technical problem is exemplified by the section " Conversion of Oleic Acid into Candle Material," Vol. III. Chap. XV.

CHAPTER XII

EXAMINATION BY STRICTLY SCIENTIFIC METHODS

If the information obtained by the methods described in the foregoing chapters is not deemed sufficient for elucidating the composition of a given product, recourse must be had to strictly scientific methods. As a rule, these do not fall within the province of the technical analysis of oils, fats, and waxes.

Many of the analytical processes described in the foregoing chapters have passed through the stage of a strictly scientific research, before they were worked out so far that they can be regarded as expeditious technical methods. Since not infrequently it becomes necessary to undertake further research, I collate in this chapter a number of methods which at present may be termed strictly scientific. It appears also useful to record in this chapter some proposed methods which, so far, have not led to useful results, but are apt to offer hints and suggestions for further elaboration.

A. Examination of Glycerides

(*a*) *Fractional Crystallisation of Glycerides*

It has been pointed out already that the natural oils and fats are more or less complicated mixtures of several triglycerides; recent researches have shown (Chap. I.) that mixed triglycerides form the preponderant constituents of the natural oils and fats, and their occurrence must be more seriously taken into account than has been done hitherto.[1] The mixed glycerides described Chap. I. have been isolated by fractional crystallisation. Not until a well-crystallised substance has been obtained, will ultimate (elementary) analysis furnish any useful indications. This becomes apparent on glancing at the following table stating the percentages of carbon, hydrogen, and oxygen contained in palmitin, stearin, olein, linolin, ricinolein, in some mixed glycerides, and in a number of commercial oils and fats.

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[1] Cp. Lewkowitsch, "Les Corps gras (Industrie et Analyse) Conférence," *Bullet. Soc. Chim. de France*, April 1909.

Simple Triglycerides.	Formula.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Palmitin . . .	$C_{51}H_{98}O_6$	75·93	12·16	11·91
Stearin . . .	$C_{57}H_{110}O_6$	76·85	12·36	10·79
Olein . . .	$C_{57}H_{104}O_6$	77·38	11·76	10·86
Linolin . . .	$C_{57}H_{98}O_6$	77·90	11·16	10·94
Ricinolein . .	$C_{57}H_{104}O_9$	73·39	11·16	15·45

Mixed Triglycerides.	Formula.	Mol. W.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Stearodipalmitin .	$C_{53}H_{102}O_6$	834·82	76·18	12·32	11·50
Palmitodistearin .	$C_{55}H_{106}O_6$	862·85	76·49	12·38	11·13
Stearodiolein . .	$C_{57}H_{106}O_6$	886·85	77·13	12·05	10·82
Oleodistearin . .	$C_{57}H_{108}O_6$	888·86	76·95	12·25	10·80

Oil or Fat.	Carbon. Per cent.	Hydrogen. Per cent.	Oxygen. Per cent.
Linseed oil[1]	76·80	11·20	12·00
" "	77·80	11·20	11·80
" "	78·00	11·00	11·00
Rape oil[1]	77·99	12·03	9·98
"	78·20	12·08	9·72
"	77·91	12·02	10·07
Finback oil[2]	77·05	12·05	10·90
Train oil[2]	76·85	11·80	11·35
Cod liver oil[2]	75·91	12·22	11·87
Seal oil[2]	77·10	13·50	9·40
Horse fat[1]	77·07	11·69	11·24
Lard[1]	76·54	11·94	11·52
Beef tallow[1]	76·50	11·91	11·59
Mutton tallow[1] . . .	76·61	12·03	11·36
Butter fat[1]	75·63	11·87	12·50
" "[3]	74·78	11·46	13·76

Beckmann,[4] as also *Normann*[5] attempted to determine the mean molecular weights of oils and fats by the cryoscopic and ebullioscopic methods, but it was found that the molecular weights so obtained for the glycerides are not in accordance with those derived from the saponification values, as will be gathered from the following table due to *Normann* (cp. also Vol. III. Chap. XV. "Polymerised Tung Oil"):—

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[1] First analysed by Saussure in 1820, *Annal. Chim. et Phys.* 13, 351; Schulze and Reinecke, *Liebig's Annalen*, 142, 198; König, *Chemische Zusammensetzung der Nahrungsmittel*, etc., i. 199, 200, 429.

[2] Schaedler, *Technologie der Fette und Öle*, p. 750.

[3] Fleischmann and Warmbold, *Zeits. f. Biolog.* 50 (1907), 305.

[4] *Forschungsberichte über Lebensmittel*, 1894, i. 422; 1895, ii.

[5] *Chem. Zeit.*, 1907, 311.

Oil.	Saponific Value.	Molecular Weight.	
		Calculated.	Found.
Olive oil	190	904·7	834-1078
Rape oil	180·5	930·7	699·9-993·4
Rape oil (nitrobenzene solution) .	...	...	911-1248
Blown rape oil	202·7	828·8	1042-825
Castor oil	185·2	917·1	691-501

Curiously enough, *Custodis*[1] obtained by the cryoscopic method half the theoretical values in the cases of liquid α-α-dilaurin and liquid trilaurin.

Later cryoscopic and ebullioscopic experiments were carried out by *Held*[2] in a solution of (dry) ethylenedibromide. It was found in the case of the cryoscopic determinations that with the increase of the amount of substance the molecular weights increased, as will be gathered from the following table :—

Cryoscopic Determinations of Molecular Weights in (dry) Ethylenedibromide

Substance.	Molecular Weight.	Amount of Substance employed.
		Grms.
Olive oil	829·5-948·5	0·445 -2·2886
Castor oil	827·8-1063	0·181 -1·6860
Cacao butter . . .	867 -1003	0·3637-1·9585
Japan tallow . . .	927 -2284	0·2546-0·9292
Mutton tallow . . .	870 -1267	0·2590-2·4442
Oleodistearin . . .	897·7-898·2	0·1415-0·6224
Triolein	895·7-904·8	0·3188-1·7091
Oleic acid . . .	425·5-587·2	0·2196-1·2496

Although in the case of oleodistearin and triolein approximately correct numbers were obtained, much less satisfactory or, indeed, useless numbers were found in the other cases. Glycerides of saturated fatty acids and the higher saturated fatty acids exhibited such small solubilities that ethylenedibromide was found entirely unsuitable. Equally unsatisfactory results were obtained in ebullioscopic experiments, when ethylenedibromide was used as a solvent. This may be illustrated by the following table :—

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[1] *Inaug. Dissert.*, Zürich, 1909.

[2] *Inaug. Dissert.*, 1909, Liebertwolkwitz ; cp. also Dankworth, *Inaug. Dissert.*, 1906, Leipzig.

Ebullioscopic Determinations of Molecular Weights in Ethylenedibromide

Substance.	Molecular Weight.	Concentration.
		Per cent.
Olive oil	649-598	1·13-6·47
Castor oil	768-643	1·23-5·43
Cacao butter . . .	752-642	1·46-8·28
Japan tallow . . .	806-643	0·91-9·30
Mutton tallow . . .	670-556	1·56-9·00
Tristearin	755-683	0·844-6·18
Triolein	822-700	1·47 -6·79
Tripalmitin . . .	802-726	0·925-5·28
Stearic acid . . .	304-346	0·975-3·25
Oleic acid . . .	248-370	0·931-7·76
Palmitic acid . . .	297-333	0·876-3·62

As an illustration of the practical application of these methods to a commercial product the following numbers, due to *Held*, may be reproduced :—

Cryoscopic Determination of the Molecular Weights of Linseed Oil, Polymerised Linseed Oil, and their Fatty Acids, in Benzene

Substance.	Molecular Weight.	Weight of Substance employed.
Oils—		Grms.
Linseed oil	699·8 (through 701·2)-686·8	0·1482-2·0091
Polymerised linseed oils		
I. By heating to 310°-315° C. for one hour	1170-1196	0·3557-1·3616
II. By blowing with air at 310° C. for 3 hours	1485-1527	0·5591-2·2501
Fatty Acids from—		
Linseed oil	545·6-561·2	0·8270-1·6607
Polymerised linseed oil .	836·2-849·2	0·5521-1·8254

The experiments undertaken by *Heintz* to obtain pure *stearin*[1] from tallow by repeated crystallisation from ether did not, in his hands, lead to chemically pure substances. His method has been employed with greater success in the preparation of a number of mixed glycerides (described in Chap. I.). The first mixed glyceride was obtained by precipitating the ethereal solution of mkányi fat by alcohol (*Heise*). *Holde*,[2] in an examination of olive oil, cooled the ethereal solution to −40° to −45° C. Other methods for the resolution of oils and fats into their component glycerides are based on the crystallisation from a mixture of chloroform and ether (*Fritzweiler*), or from acetone,[3]

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[1] Pure stearin was first prepared by *Chevreul*.

[2] *Berichte*, 1901, 2402.

[3] Cp. Breda, German patent 144,868.

(*Klimont*), or from a mixture of chloroform and acetone (*Seitter*[1]). *Kreis and Hafner*[2] then showed that it was impossible to obtain glycerides free from olein or from mixed glycerides containing oleic acid by mere crystallisation from alcohol, ether, benzene, and amyl alcohol.[3] Olein so tenaciously adheres to the saturated glycerides that although the recrystallised glyceride retains its melting point unaltered, it still absorbs iodine. The impurity can, however, be removed by treating the glyceride with *Hübl's* solution (or with *Wijs'* solution) so as to convert the oleo-glyceride into its chloro-iodo-compound. The latter can then be more readily removed by crystallisation from benzene or alcohol, and finally from ether.

The foregoing methods appear to be full of promise for the successful resolution of the mixtures of glycerides, with which we have to deal in the natural oils and fats. Up to a few years ago hardly more than a beginning had been made. Recently, however, *Bömer*[4] worked out a method for the identification of pure glycerides which is based on the exact determination of the melting point. The individuality of a glyceride can be established by recrystallising a substance in such a manner that only so much of the solvent at a low temperature is employed that by far the largest portion of the substance separates, and by continuing the recrystallisation twenty or thirty times until no more crystals separate. If it be found that both the glycerides dissolved in the several mother liquors and the crystals obtained therefrom have in each case the same melting point, the assumption is justified that a chemical individual has been obtained.[5]

Bömer[6] found that a mixture of two molecules of tristearin and one molecule of tripalmitin can be easily resolved into its constituents by crystallisation from ether; also a mixture of one molecule of tristearin and of two molecules of tripalmitin can be resolved, although not quite so readily, into its constituents.

In the case of mixed glycerides, however, which, as stated already, form the preponderant portion of most oils and fats, the problem offers very great difficulties. This becomes obvious if we remember that, *e.g.*, assuming that no other fatty acids than palmitic, stearic, and oleic are present, in tallow we may *a priori* expect to find the following ten glycerides:—

Tripalmitin, tristearin, triolein, dipalmitostearin, dipalmitoolein, palmitodistearin, palmitodiolein, palmitostearoolein, distearoolein, stearodiolein.

For examples of the most tedious and very laborious work entailed in the crystallisation of natural fats until pure products are obtained the reader must be referred to *Bömer's* papers in which the isolation of tristearin, palmitodistearin, and dipalmitostearin from tallow and the isolation of stearodipalmitin and palmitodistearin from lard is described.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 486. [2] *Berichte*, 1903, 1126.

[3] Cp. also H. Okada, *Chem. Zeit.*, 1908, 1199.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 90; *ibid.*, 1913, xxv. 321. Cp. also Chap. I. p. 35, and Chap. V. p. 317.

[5] If the unsaturated glycerides have been removed by iodochloride, the absence of halogens in the final product must be ascertained.

[6] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 97; 1908, xv. 82; 1909, xvii. 355.

The melting point of the crystallised glyceride is first determined in a melting-point tube (cp. Chap. V. p. 319). After the substance has melted, the thermometer, with the attached melting-point tube, is taken out of the sulphuric acid and immersed immediately—for about ten seconds—in water at the temperature of 15° C. The thermometer and melting-point tube are then placed in another sulphuric acid bath at the ordinary temperature; the bath is immediately heated. As soon as the sulphuric acid has reached a temperature within a few degrees of the "point of transition," the source of heat is removed and the temperature observed carefully whilst the sulphuric acid is stirred constantly. That temperature at which the substance in the melting-point tube has become translucent, or perfectly transparent, is noted as the "point of transition." When the temperature of the sulphuric acid bath rises further, the substance becomes more and more cloudy and at last completely opaque. As the source of heat has been removed (as described above) the temperature will only rise about 5° above the "transition point," and then begins to fall. After the temperature has been allowed to fall to about the "transition point"—which requires some five to ten minutes—the sulphuric acid bath is again heated with constant stirring, and the point is now observed carefully at which the substance becomes completely clear and liquid. This point is considered to be the "melting point" of the glyceride which has solidified from the once melted substance. For a number of diagrams illustrating the changes in the appearance of the substance during these observations, the reader must be referred to the original papers.[1]

(*b*) *Fractional Distillation of Glycerides*

The glycerides of the lower fatty acids can be fractionally distilled in a complete vacuum without undergoing decomposition, as has been shown first by *Chevreul*.

On distilling *laurel oil* in a complete vacuum *Krafft*[2] found that at 260°-275° C. a product was obtained, melting at 43° C. and yielding after crystallisation from alcohol a substance melting at 45° C. and agreeing in its elementary composition with trilaurin. On distilling *nutmeg butter* in the vacuum of the cathode light, a distillate was obtained between 290°-300°, solidifying at 53° and melting after recrystallisation from alcohol at 55°. Elementary analysis showed that the substance consisted of trimyristin. In both cases impurities had been removed by the process of recrystallisation. Inasmuch as laurel oil and nutmeg butter consist preponderantly of glycerides of lauric acid and myristic acid respectively, the proportion of mixed triglycerides in the natural fats cannot be large; hence intra-molecular changes as may be expected in the case of natural oils and fats, consisting preponderantly of mixed triglycerides, cannot have occurred.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 97; 1909, xvii. 363.

[2] *Berichte*, 1903, 4343.

On subjecting *Japan wax* to the same process, palmitin underwent decomposition. Inasmuch as *Krafft* ascertained that pure tripalmitin distils in the vacuum of the cathode light at 310°-320° C., it may be conjectured that the other constituents of Japan wax (dibasic acids, etc.) were the cause of the failure to obtain pure tripalmitin by distillation.

It would, therefore, seem that whereas pure tripalmitin, as also pure stearin and olein (*Chevreul*), can be distilled without decomposition *in vacuo*, that the impurities in natural oils and fats are largely contributary to secondary products being formed.

As an analytical method the fractional distillation of such fats as tallow, etc., would seem to be a hopeless method. Very much better results are obtained by fractional distillation of the methylesters of the fatty acids (see below).

B. Examination of the Fatty Acids

(*a*) *Examination of the Volatile Fatty Acids*

The process described in Chapter VIII. p. 529 permits to distil off all the volatile acids contained in and derived from natural oils and fats, and thus to separate them almost completely from the insoluble acids.

The amounts of potassium hydrate required to saturate the total volatile acids in a number of oils and fats have been given in the table on p. 530. The neutralised distillate is then boiled down to a small volume, and the bulk of the volatile acids is liberated as an oily layer by adding to the solution of the potassium salts fairly concentrated sulphuric acid. In order to recover the last traces of the most volatile acids, the aqueous acid layer may again be subjected to distillation or may be extracted with ether.

According to *Liebig*, the aqueous solution of the volatile fatty acids is divided into two equal portions. One part is exactly neutralised by caustic potash; the second part is then added, and the whole subjected to distillation. The acids of lower boiling points pass into the distillate, whilst the higher boiling acids remain in the distilling flask as potassium salts. Acetic acid, however, if present, also remains behind as potassium salt. By repeatedly treating both the distilled and the remaining acids in the same manner, pure fractions of the several acids are finally obtained. *Liebig* employed this method for separating butyric acid from a mixture of butyric and isovaleric acids, and, further, for isolating acetic acid in admixture with either of these two acids. *Veiel*, however, arrived at the opposite result, having found that isovaleric acid distilled over, whereas butyric acid remained behind. *Lieben* (by stating that *Liebig's* method is not accurate) partly confirmed *Veiel's* results, and effected an approximately satisfactory separation by partially neutralising the mixture of acids, when the higher acids could be distilled off, whilst the lower acids remained behind as salts. *Wechsler*,[1] applying *Lieben's* method to equivalent amounts of two acids, examined the following mixtures: formic and acetic; acetic and propionic; acetic and butyric; acetic and isobutyric; propionic and butyric; butyric and caproic. The mixed acids were neutralised with four-fifths of the theoretical amount of alkali, and distilled as long as the distillate was found to be acid. The remaining salts were then treated with an amount of sulphuric acid sufficient to liberate exactly three-fifths of the fatty acids, and distilled again. The last fifth was finally obtained by acidulating the residue and subsequently distilling it. The first fraction was found to contain the higher acid,[2] and the last fraction the lower acid, in an almost pure state. The mixture of butyric and isovaleric acids, however, could not be separated by this method, a result at variance with the statements of both *Liebig* and *Veiel*. *Crossley*,[3] again, could not obtain such satisfactory results as *Wechsler's* statements led to expect. On distilling fermented wool-scouring liquors, *A. and P. Buisine*[4] found that the volatile fatty acids with a higher number of carbon atoms distilled over first.

Erlenmeyer and Hell[5] proposed to separate the several volatile acids by fractional saturation with silver carbonate. The acids, having a higher boiling point, are precipitated first.

Fitz[6] showed that by mere fractional distillation of the free acids in a current of steam, if care be taken to replace the water as it is distilled off, a separation can be effected, the acid of higher molecular weight passing over first. This result has been corroborated by *Hecht*[7] (cp. also Chapter III.[8]).

The examination of the volatile acids has received a new impetus through the methods of *Müntz and Coudon*, and of *Polenske* (Chapter VIII.). It is therefore advisable, in the examination of the volatile fatty acids, to separate them into soluble volatile acids and insoluble volatile acids, as detailed above (Chapter VIII. p. 532). Further important suggestions as to these examinations are contained in papers by *Kirschner*,[1] *O. Jensen*,[2] *K. Jensen*,[3] and also by *Wijsman and Reijst*.[4] These methods may perhaps lead to the quantitative determination of caprylic acid in the form of its silver salts.[5]

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[1] *Journ. Soc. Chem. Ind.*, 1894, 179; cp. also Sorel, *ibid.*, 1896, 15 (543), 143.

[2] Cp. *Analyst*, 1907, 201.

[3] *Proc. Chem. Soc.*, 1897, 21.

[4] *Chem. Centr.*, 1898, 23.

[5] *Liebig's Annal.* 160. 296, footnote.

[6] *Berichte*, 11. 46.

[7] *Liebig's Annal.* 209. 319.

[8] For further information the reader may be referred to papers by Duclaux (*Ann. Phys. Chim.*, 1874 [5], 2, 289; Haberland (*Zeits. f. anal. Chem.*, 1899, 217); Chapman (*Analyst*, 1899, 114); Holzmann (*Arch. d. Pharm.*, 1898, 409); Crossley and Le Sueur (*Journ. Chem. Soc.*, 1897, 162); Crossley, *ibid.*, 1897, 580; Muspratt, *Journ. Soc. Chem. Ind.*, 1900, 207; Schütz, *Zeits. f. anal. Chem.*, 1900, 77; O. Jensen, *Annuaire agricole de la Suisse*, 1904; Lasserre, *Ann. Inst. Past.*, 1907 (21), 829, adversely criticised by Hodgson, *Analyst*, 1909, 435, and by C. A. Keane and P. Narracott, *ibid.*, 1909, 436; R. K. Dons, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1908, xv. 75, xvi. 705; A. Faucon, *Compt. rend.*, 1909 (148), 38; J. Effront, *Seventh Intern. Cong. Appl. Chem.*, Sect. iv. A1, 83, London, 1909; G. Seliber, *Compt. rend.*, 1910 (150), 1267; F. Edelstein and F. v. Csonka, *Biochem. Zeits.*, 1912 (42); K. Langheld and A. Zeileis, *Berichte*, 1913, 1171.

(*b*) *Examination of the Non-Volatile Fatty Acids*

The separation of the saturated from the unsaturated acids described Chap. VIII. p. 538 is not a quantitative one, as has been pointed out already. It appeared likely that by repeating the extraction of the lead salts in which the saturated acids preponderate, lead salts free from unsaturated acids might be obtained. This was, however, not borne out in the case of a specimen of linseed oil fatty acids examined in the author's laboratory. The fatty acids of the insoluble lead salts had the iodine value 22·34, and formed 8·9 per cent of the total fatty acids. After passing the solid fatty acids for a second time through the lead-salt-ether process, 7·5 per cent of solid acids, which still absorbed 19·2 per cent of iodine, were obtained.

Experiments made by the author with a view to removing the unsaturated acids by converting them into chloro-iodo-compounds have not led to satisfactory results.

The **solid** saturated acids can be further separated by fractional precipitation of their alcoholic solutions (saturated in the cold) with alcoholic solutions of barium or magnesium acetate in the hot (*Heintz* [6]). At first the magnesium salts of the higher fatty acids separate, then those having a lower number of carbon atoms. Each precipitate is filtered off, the free acetic acid in the filtrate is neutralised with ammonia, and then a fresh quantity of magnesium acetate is added. If the latter no longer produces a precipitate, it is in some cases possible to obtain a further precipitate by adding a concentrated aqueous solution of barium acetate.

Pebal [7] used as a precipitant an alcoholic solution of lead acetate. Every fraction is then decomposed by hydrochloric acid, and the fatty acids of the same melting point are united. The several fractions are repeatedly subjected to the same process until pure substances result. A fraction may only then be looked upon as a chemical individual, if its melting point is not altered by further recrystallisation, and if by further fractional precipitation with magnesium acetate, acids having identical melting points are obtained. Elementary analysis of the acid or of its silver salt would confirm that a chemical individual has been reached.

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[1] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1905, ix. 65.

[2] *Ibid.*, 1905, x. 266. [3] *Pharmceutisk Tidende*, 1903, 385.

[4] *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1906, xi. 267.

[5] Cp. Lewkowitsch, *Jahrbuch der Chemie*, xiv. p. 437; Vol. II. Chap. XIV. "Cocoa Nut Oil," "Butter Fat"; Vol. III. "Margarine." For "Baryta Value" cp. Second Edition of this work, 1898, p. 158; Avé-Lallemant (*Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, xiv. 317). For "Cadmium Value" cp. Paal and Amberger, *ibid.*, 1909, xvii. 45; Lührig, *Pharm. Zentralb.*, 1909 (50), 441. For Zinc Salts cp. Bremer, *Forschungsberichte*, 1897 (iv.), 6; Paal and Amberger, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1909 (xvii.), 45. For "Ethylester Value" see p. 666. For "Lauric-myristic Value" cp. W. Arnold, *Zeits. f. Unters. d. Nahrgs- u. Genussm.*, 1907, 164.

[6] *Journ. f. prakt. Chem.*, 1855 (66), 1. [7] *Liebig's Annal.* 91. 138.

It is evident that pure acids can only be arrived at by frequent repetition of the fractional precipitation. The quantitative isolation of the individual acids by this method must, however, be considered as being altogether out of the question.

Experiments made by *Hehner and Mitchell*[1] on mixtures of palmitic and stearic acids with a view to ascertaining the usefulness of such methods for analytical purposes, furnish an approximate idea as to how far separation can be effected. Pure stearic and palmitic acids were mixed in the proportions stated in the following table, and precipitated with such quantities of aqueous barium acetate solution, as were sufficient to precipitate the stated amounts of stearic acid :—

Separation effected by Precipitation of Mixed Stearic and Palmitic Acids with Aqueous Barium Acetate

Stearic Acid. Grms.	Palmitic Acid. Grms.	Barium Acetate added sufficient to precipitate Stearic Acid. Grms.	Stearic Acid in Precipitate. Per cent.
1	1	1	71·7
1	2	1	62·8
1	3	1	27·9
1	3	1	30·9
0·5	0·5	0·5	62·7
1	1	0·5	46·6

On precipitating the filtrates in a similar fashion, it not infrequently happened that the second fraction contained a larger proportion of stearic acid than did the first fraction.

Similar experiments with aqueous solutions of magnesium acetate and alcoholic solutions of lead acetate gave no better results.

Kreis and Hafner[2] suggest to determine in a mixture of stearic and palmitic acids, first, the amount of stearic acid by the method described p. 556, and then to dissolve the mixed fatty acids in so much alcohol that on cooling to 0° C. the palmitic acid (the amount of which is calculated by difference) remains in solution. After allowing to stand for twelve to fourteen hours in an ice-chest, they filter off and crystallise the residue on the filter twice from alcohol; the crystals so obtained are judged to be pure stearic acid. The filtrate, which only contains 0·12 grm. of stearic acid per 100 c.c., is evaporated down to half its volume, and mixed with so much of an alcoholic magnesium acetate solution as is required for precipitating the dissolved stearic acid. After standing for twelve to fourteen hours at the ordinary temperature, the precipitate is filtered off and the fatty acids are recovered from the filtrate. *Kreis and Hafner* found them to melt at 60° C. The acids are next dissolved in so much alcohol that they do not crystallise out at the ordinary temperature, and one-third of the previously used amount of magnesium acetate is then added. After repeating this operation once more and recrystallising from alcohol, pure palmitic acid of the melting point 62·3° C. was obtained. *Kreis and Hafner* are of the opinion that this process, in which the bulk of the stearic acid is removed at the outset by simple crystallisation, is more expeditious than *Heintz's* method.

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[1] *Analyst*, 1896, 318.

[2] *Berichte*, 1903, 2766.

Berg,[1] as also *Fahrion*,[2] suggest the separation of palmitic acid from stearic acid by means of acetone.

The above-suggested methods apply to a mixture of two acids only. *Holde*[3] has shown that whilst the separation of two acids such as stearic and palmitic, or arachidic and palmitic, can be effected by *Heintz's* method, the results become very uncertain when three acids are present.

Fractional distillation of the mixed solid acids, with a view to isolating the individual acids, did not lead to satisfactory results; nor did crystallisation from alcohol prove of advantage, chiefly because small amounts of ethylic esters are formed (*E. B. Holland*[4]).

The resolution of the mixed **liquid** fatty acids by means of fractional distillation in the vacuum of the cathode light[5] has been resorted to by *F. Krafft*.[6] Such a vacuum, for the measurement of which a mercury gauge can no longer be used, can be obtained without difficulty by the employment of a *Babo* vacuum pump. The boiling points of fatty acids recorded in Chapter III. have been determined by means of this apparatus.

Bedford, however, showed that the separation of the unsaturated fatty acids of linseed oil cannot be effected by fractional distillation *in vacuo*. Thus an experiment yielded three fractions which had respectively the iodine values 201·1, 203·8, 206·6.

The somewhat complicated contrivance described by *Krafft* may be advantageously replaced, in a technical laboratory, by a combination of two apparatus (Fig. 58 and Fig. 59), designed by the author[7] for fractional distillation *in vacuo*. As they have been found very convenient in daily use, they may be recommended to laboratories having a vacuum pipe provided with several taps.

A finely drawn out tube is soldered in the distilling flask (Fig. 58). The tube is fitted on its outer end with an india-rubber tube and a screw-clamp, by means of which a current of air or of an indifferent gas can be drawn in, whilst at the same time the pressure is regulated accurately. By means of this contrivance it is also feasible to prevent frothing of the liquid. Nozzle *a* of the adapter (Fig. 59) is fitted to a *Liebig* condenser; *b* and *c* are connected by india-rubber tubing with two taps of a vacuum pipe. On starting the distillation, the distilling flask, the adapter, and the conical receiving flask are exhausted through *b* and *c*, whilst the stopcock *d* remains open. When the first fraction has distilled over, tap *d* and the vacuum tap connected with *c* are closed. The receiving flask is thus shut off from the vacuum pipe, and is filled with air by disconnecting the india-rubber tubing from *c*. The flask can be taken off easily and emptied, or replaced by another, whilst the distillation proceeds without interruption. When the receiving flask is fitted on again it is exhausted through *c*, as before, and then connected with the distilling flask by opening tap *d*.[1]

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[1] *Chem. Zeit.*, 1908, 779.

[2] *Zeits. f. angew. Chem.*, 1909, 771.

[3] *Berichte*, 1905, 1250.

[4] *Journ. Ind. Eng. Chem.*, 1911, 170; cp. also Vol. II. Chap. XIV. "Almond Oil"; "Apricot Kernel Oil."

[5] *Berichte*, 1896, 1316, 2240; 1899, 1623; 1903, 1690.

[6] *Berichte*, 1883, 1726; 1889, 816; 1895, 2583; *Journ. f. prakt. Chem.*, 1909 (80), 242; cp. also Fischer and Harries, *Berichte*, 1902, 2158; E. Erdmann, 1903, 3456.

[7] *Journ. Chem. Soc.*, 1889, Trans. 360.

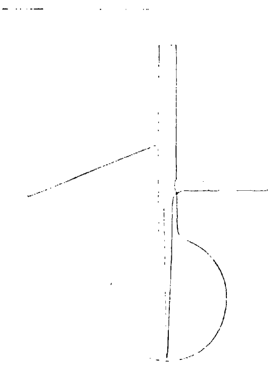
Fig. 58.

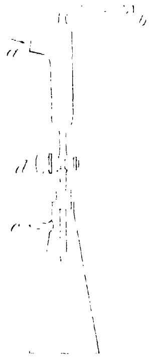

Fig. 59.

A much more promising process than the fractional distillation of the fatty acids themselves is the fractional distillation of the methylic and ethylic esters of the fatty acids.[2]

Haller[3] fractionates the **methylesters**[4] obtained by "methanolysis"

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[1] For similar adapters cp. *Berichte*, 1887, 1833; Bedford, *Inaug. Dissert.*, Halle a/S, 1906; *Chem. Zeit.*, 1908, 487. Freundlich, *Chem. Zeit.*, 1908, 820, suggests replacing the adapter and receiver shown in Fig. 59 by a pair of interchangeable adapters, thus following closely the device which is employed in works where distillation *in vacuo* is carried out. A. Hahn, *Berichte*, 1910, 1725; J. Campbell Brown, *Proc. Chem. Soc.*, 1910, 149; cp. also *Chem. Zeit.*, 1909, 27; *Zeit. f. angew. Chem.*, 1909, 15.

[2] Cp. Third Edition of this work, 1904, p. 422.

[3] *Compt. rend.*, 1906 (143), 694.

[4] H. Meyer and A. Eckert (*Monatsh.*, 1910, 1232) prepare the methylesters by heating the lithium salts of the mixed fatty acids with thionylchloride and extracting the chlorides thus obtained with boiling methylalcohol.

(see Chap. II. p. 100) under ordinary pressure up to a temperature of 194° C. (which is the boiling point of methyl caprylate) and beyond 194° C. *in vacuo.* The fractional separation proceeds satisfactorily up to methyl laurate ; beyond that the separation becomes less complete, especially as the esters of the higher saturated acids—myristic, palmitic, stearic—always retain oleic ester. This method has been applied to the investigation of castor oil, linseed oil, cocoa nut oil, cotton seed oil, Japan wax, and Cäy-Cäy fat (cp. Vol. II. Chap. XIV. under the headings of these oils and fats).

The method is carried out as follows (*Haller*[1]) :—500 grms. of fat are mixed with 625 grms. of absolute methyl alcohol containing 2·5 per cent of hydrochloric acid and 850 grms. of ether. The mixture is heated under a reflux condenser for twelve hours. After cooling, the liquid is treated with barium carbonate in order to neutralise the free acid, and is then washed with brine in order to remove glycerin and the excess of methyl alcohol. The ethereal layer is next dried over calcium chloride, and warmed in order to distil off the ether. The remaining methylesters are then fractionated *in vacuo.* The residue remaining in the flask is a black solid mass ; in various operations 5-30 grms. of this residue were obtained. The different fractions are cooled below the freezing point, so as to recover solid esters which are retained by the liquid esters, in the form of crystals.

Unfortunately the boiling points of the methylesters of the unsaturated acids lie so closely together, that the esters cannot be separated from each other by fractional distillation, as will be seen from the following table detailing the result of a fractional distillation of those methylesters of the cotton seed oil fatty acids which boil above 200° C. at a pressure of 18 mm. :—

Fraction.	Boiling Point. °C.	Pressure.	Quantity obtained from 535 Grams of Oil.	Iodine Value.[2]
I. . .	Up to 201·5	16 mm.	8 grams.	77·13
II. . .	201·5-204	16 ,,	9 ,,	101·19
III. . .	204-207·5	16 ,,	20 ,,	123·51
IV. . .	207·5-210·5	16 ,,	83 ,,	130·87
V. . .	210·5-214·5	16 ,,	11 ,,	123·83
VI. . .	Above 214·5	16 ,,	2 ,,	107·23
			133 ,,	

As an example of an examination of cod liver oil acids by this method, the table published by *Bull*[3] may be reproduced :—

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[1] *Compt. rend.*, 1908 (146), 250.

[2] The iodine values of the methylesters of oleic, linolic, and linolenic acids are respectively 85·8 and 172·8 and 260.

[3] Bull, *Berichte*, 1906, 3570.

Fraction up to °C.	Per cent.	Saponification Value.[1]	Iodine Value.	Fraction up to °C.	Per cent.	Saponification Value.	Iodine Value.
161·5	0·45	...	...	200·0	1·18	195·2	86·2
163·0	2·00	229·5	9·5	202·5	2·10	196·5	97·6
165·0	1·00	227·8	9·2	205·0	3·88	189·9	101·8
170·0	0·65	221·5	26·1	206·0	17·00	188·1	100·6
175·0	0·90	216·2	39·4	210·0	2·25	186·8	123·4
177·5	0·35	214·4	44·8	212·5	0·65	182·8	143·3
180·0	0·90	211·4	62·2	215·0	0·65	181·2	158·2
183·5	2·40	209·2	63·3	217·5	1·25	179·0	168·7
185·0	4·05	207·1	62·2	220·0	1·20	176·0	167·4
186·0	7·48	204·6	57·2	223·0	5·12	174·0	156·2
187·0	1·83	206·5	50·5	225·0	9·26	173·2	152·2
188·0	1·37	204·6	50·2	227·5	0·66	170·2	155·7
190·0	1·69	202·5	56·8	230·0	0·88	167·8	144·0
192·5	0·91	201·1	64·5	235·0	0·90	163·2	143·6
195·0	0·44	199·2	59·3	239·0	1·30	160·4	138·4
197·5	0·76	197·3	...	240·0	3·52	159·8	130·0

For experiments made by *Tsujimoto* with methylesters of fatty acids from marine animal oils cp. [2] Vol. II. Chap. XV.

Fendler[3] suggested, for the detection of small quantities of cocoa nut oil and palm nut oil in butter fat, to distil the **ethylesters** under ordinary pressure up to 300° C., on the assumption that only the esters of the lower fatty acids, up to and including the ethylester of myristic acid, would distil over. The volume of the esters obtained from 85 grms. of fat are measured. Thus butter fats gave from 2·5 to 6·1 c.c., palm kernel oil 37 c.c., and cocoa nut oil 40 to 42 c.c. For the minute details which must be observed in the carrying out of this method so as to obtain comparable results, the reader is referred to the original paper. It is hardly likely that this method, which has been specially designed for the rapid detection of an admixture of palm nut oil or cocoa nut oil to butter, will supersede other proved methods (see Vol. II. Chap. XIV. "Butter Fat"). *Fendler* proposes the name "distillation value" for the number of c.c. of ethylesters obtained. It need only be added that *Fendler* saponifies in the cold according to *Henriques*' directions (see p. 106), substituting, however, alcoholic potash for alcoholic soda.

Krafft and his collaborators consider, as the best method for the identification of fatty acids having a high number of carbon atoms, the conversion of the fatty acids into their corresponding hydrocarbons, the chemical and physical characteristics of which can be determined readily. The method consists in mixing thoroughly one part of acid with five parts of dry, finely-powdered barium hydroxide and then distilling *in vacuo*. Thus erucic acid, $C_{22}H_{42}O_2$, yields heneicosylen, $C_{21}H_{42}$, boiling at 201°-202° C. under 12 mm. pressure, and melting at about + 3° C.; from it is obtained a dibromide which was reduced by means of hydriodic acid and red phosphorus to normal heneicosane melting at 40° C. The usefulness of this method has been especially demonstrated in the investigation of the dibasic acids occurring in Japan wax (see Vol. II. Chap. XIV.).

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[1] The saponification values of the methylesters of myristic, palmitic, oleic, gadoleic, and erucic acids are respectively 231·4, 207·4, 189·2, 172·8, and 160·9.

[2] Cp. also *Chem. Revue*, 1913, 8.

[3] *Mitt. a. d. Pharm. Institut der Univ.*, Berlin, 1908. The author states that the method was worked out in 1903. Cp. also J. Hanus and F. Petrik, *Chem. Zeit. Rep.*, 1907, 205.

For the detection and examination of the highly unsaturated fatty acids in cod liver oil, *Bull*[1] proposed fractional crystallisation of their sodium and potassium salts from alcohol and ether. He thus obtained fatty acids, the high iodine values of which (322 and 347) indicated the presence of acids belonging to the series $C_nH_{2n-8}O_2$ (cp. Vol. II. Chap. XIV. "Cod Liver Oil"). For further information the reader must be referred to the original paper, since *Bull* himself controverts, and throws doubts on, some of his own results.[2]

Tortelli and Fortini suggest the determination of the temperature at which the separation of crystals of sodium salts of the liquid fatty acids, takes place with a view to recognising individual fatty acids (cp. Chap. III. p. 131, footnote 1). The observations made by them were added to the table given above, Chap. VIII. p. 553; in view of the great uncertainty attaching to this suggested method, the reader must be referred to the original.[3]

C. Examination of the Unsaponifiable Matter

The exhaustive examination of the unsaponifiable substances demands the preparation of considerable quantities so that the separation of the sterols from the hydrocarbons and other unsaponifiable substances can be carried out effectively. The first step consists in the treatment by the digitonin method or in treatment with low boiling petroleum ether at a low temperature, whereby the sterols and aliphatic alcohols can be freed from the bulk of the resinous and colouring substances.

From the mixture of sterols and aliphatic alcohols the individual alcohols may be isolated by first crystallising fractionally their benzoic or acetic esters. The latter are easier to distil than the original substances, and can therefore be more effectively resolved into fractions. The indications given in Chap. IX. will assist the analyst in working out a suitable *modus operandi*.

The petroleum ether insoluble substances represent frequently a viscous liquid, which has been resolved, in some cases, into its components by fractional distillation. *Matthes* and his collaborators have devoted attention to this subject, but hitherto, owing to the difficulty of the problem, which naturally varies with each different oil and fat, a general method has not been worked out. As an example may be given the following table, detailing the results of the fractional distillation of the liquid portion of the unsaponifiable matter from cheiranthus oil (*Matthes and Boltze* [1]).

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[1] *Chem. Zeit.*, 1899, 996; 1043. [2] *Ibid.*, 1900, 814.
[3] *Chem. Zeit.*, 1910, 690.

Fraction.	Iodine Value.	Refractive Index at 40° C.
I. Up to 160° C.	193·9	1·4910
II. 160-205	89·4	1·4734
III. 205-210	119·6	1·4900
IV. Residue	112·1	1·5105

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[1] *Arch. d. Pharm.*, 1912, 250, 211 ; cp. also Matthes and Heintz, *ibid.*, 1909, 247, 161 ; Matthes and Dahle, *ibid.*, 1911, 429.

END OF VOL. I

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